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Redetermination of Monoclinic $VOHPO_4.2H_2O$

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Abstract

Single crystals of monoclinic α-$VOHPO_4.2H_2O$, α-oxovanadium(IV) hydrogen phosphate dihydrate, were synthesized by hydrothermal reaction. The structure was refined with good accuracy ($R = 0.018$) and the results are compared with those of an earlier structure determination from X-ray powder data [Le Bail *et al.* (1989). *Eur. J. Solid State Inorg. Chem.* **26**, 419–426]. Significant differences in bond lengths were found. The structure consists of vanadyl hydrogen phosphate layers running along [100]. The layers are connected *via* hydrogen bonds.

Comment

The compounds of the system $VOHPO_4.nH_2O$ (n = 0, 0.5, 2, 4) are of great interest as precursors for commercial catalysts used in the selective oxidation of butane to maleic anhydride (Centi, 1993). These compounds have therefore been studied extensively in the past few decades. The structures of $VOHPO_4.4H_2O$ and $VOHPO_4.0.5H_2O$ have been determined by Leonowicz *et al.* (1985) using small single crystals.

Until now, it was not possible to prepare crystals of α-$VOHPO_4.2H_2O$ of sufficient size for single-crystal structure analysis. Le Bail *et al.* (1989) determined the structure from X-ray powder data. The position of the H atom was calculated from neutron data. It is remarkable that in this structure determination, the P—O distances in particular deviate considerably from the values found in other monohydrogen phosphate structures.

We have redetermined the crystal structure of α-$VOHPO_4.2H_2O$ using a single crystal obtained by a new preparation procedure as described below. A comparison of our results with those of Le Bail *et al.* (1989) confirms the basic structure. However, differences in bond lengths are revealed, arising from the higher accuracy of the present work. For the discussion, atoms in the structure are labelled in the same manner as in the paper of Le Bail *et al.* (1989).

The structure of monoclinic α-$VOHPO_4.2H_2O$ consists of distorted VO_6 octahedra and $PO_3(OH)$ tetrahedra, forming layers stacked along [100]. Each VO_6 octahedron is connected by three common O atoms (O1, O2 and O3) to three $PO_3(OH)$ tetrahedra and shares two O atoms (O6 and O6′) with the neighbouring octahedra. In this way, $(VO_5)_\infty$ zigzag chains are formed running along [010]. In a pair of adjacent chains, octahedra are linked alternatively by one and two $PO_3(OH)$ tetrahedra, building up layers parallel to the (100) plane. The layers are connected *via* four types of hydrogen bond, starting at O4 (OH group), O5 and O7 (water O atoms), and all passing through the water molecule (O7) located between the layers. The four equatorial V—O bond distances vary between 1.954 (1) and 2.043 (1) Å. The longest bond involves a water O atom (O5). The two apical O atoms, O6 and O6′, have V—O distances of 1.609 (1) and 2.341 (1) Å, respectively. The first of these is a typical bond distance for an oxovanadium(IV) cation, as found in other $(VO)^{2+}$ compounds (Boudin *et al.*, 1996). The O atom with the longest V—O bond also forms part of the V═O group of the neighbouring vanadium polyhedron in the $(VO_5)_\infty$ chain. The P—O bond lengths are between 1.509 (1) and 1.528 (1) Å, and the P—OH bond distance is 1.577 (1) Å, similar to the bond distances found in other monohydrogen phosphates (Leonowicz *et al.*, 1985). A comparison of the P—O and V—O bond distances with those of Le Bail *et al.* (1989) (Table 2) reveals major differences, up to more than 12 standard deviations. We conclude that the

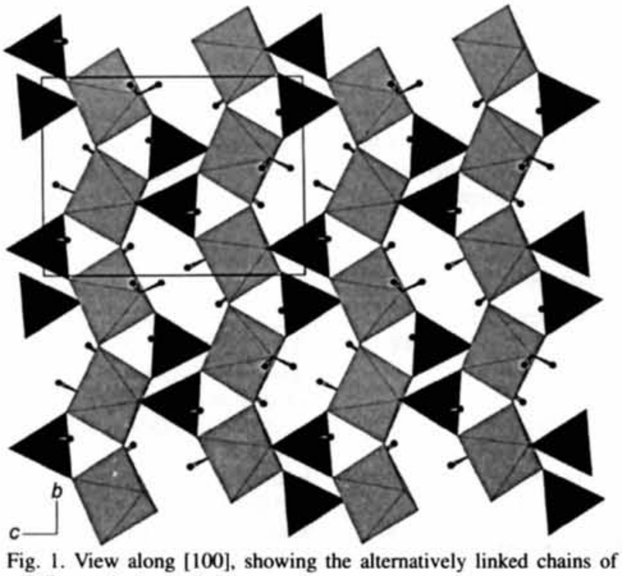

Fig. 1. View along [100], showing the alternatively linked chains of VO_6 octahedra in the layer.

bond distances from the powder structure determination should be considered with caution.

Experimental

A mixture of 12 ml of 85% H_3PO_4, 32 ml of H_2O, 15 g of oxalic acid and 14.5 g of V_2O_5 was boiled and stirred for 6 h, and the solution concentrated to a weight of 72 g. A Teflon-lined autoclave was filled with the dark-blue solution and sealed. The autoclave was heated to 363 K and kept at this temperature for two weeks. The autoclave was then air-quenched to room temperature. The crystals were filtered off, washed with water and dried at 323 K. The concentration of vanadium and phosphate ions in the solution and the reaction temperature are important parameters for the synthesis of the title compound.

Crystal data

$VOHPO_4.2H_2O$
$M_r = 198.95$
Monoclinic
$P2_1/c$
$a = 7.597$ (2) Å
$b = 7.422$ (1) Å
$c = 9.466$ (2) Å
$\beta = 95.47$ (3)°
$V = 531.3$ (2) $Å^3$
$Z = 4$
$D_x = 2.487$ Mg m^{-3}
$D_m = 2.479$ (3) Mg m^{-3}
D_m measured by pycnometry

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–18°
$\mu = 2.139$ mm^{-1}
$T = 293$ (2) K
Prismatic
0.18 × 0.13 × 0.10 mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968) *via MolEN* (Fair, 1990)
$T_{min} = 0.736$, $T_{max} = 0.807$
5980 measured reflections
1554 independent reflections

1405 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 30°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.046$
$S = 1.119$
1553 reflections
103 parameters
All H-atom parameters refined freely
$w = 1/[\sigma^2(F_o^2) + (0.0219P)^2 + 0.2446P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.367$ e $Å^{-3}$
$\Delta\rho_{min} = -0.330$ e $Å^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0150 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

U_{iso} for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
V	0.47583 (3)	0.14693 (3)	0.24294 (2)	0.00918 (7)
P	0.71860 (4)	0.15044 (4)	−0.01271 (3)	0.00895 (8)
O1	0.69442 (12)	0.13399 (13)	0.14468 (9)	0.01234 (17)
O2	0.62124 (13)	0.18385 (12)	0.42377 (10)	0.01402 (18)
O3	0.32805 (12)	0.02016 (12)	0.09453 (10)	0.01462 (19)
O4	0.92307 (13)	0.18722 (15)	−0.01210 (11)	0.0177 (2)
O5	0.28260 (14)	0.08682 (15)	0.37142 (11)	0.0175 (2)
O6	0.57351 (13)	−0.14677 (12)	0.29533 (10)	0.01454 (18)
O7	−0.02456 (15)	−0.08323 (18)	0.26944 (13)	0.0242 (2)
H1	−0.031 (4)	−0.151 (3)	0.330 (3)	0.049 (8)
H2	−0.109 (3)	−0.034 (3)	0.255 (3)	0.040 (7)
H3	0.312 (3)	0.039 (3)	0.447 (3)	0.047 (7)
H4	0.189 (3)	0.041 (3)	0.340 (2)	0.042 (6)
H5	0.957 (3)	0.170 (3)	−0.087 (3)	0.045 (7)

Table 2. *V—O and P—O bond lengths (Å)*

	This work	Le Bail *et al.* (1989)
V—O6^i	1.609 (1)	1.601 (4)
V—O3	1.954 (1)	1.898 (4)
V—O2	1.966 (1)	1.954 (4)
V—O1	1.982 (1)	1.961 (4)
V—O5	2.043 (1)	2.047 (4)
V—O6	2.341 (1)	2.347 (4)
P—O3^{ii}	1.509 (1)	1.572 (5)
P—O1	1.523 (1)	1.566 (4)
P—O2^{iii}	1.528 (1)	1.560 (5)
P—O4	1.577 (1)	1.608 (4)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H1$\cdots$O4^i	0.77 (3)	2.20 (3)	2.9045 (17)	154 (3)
O7—H2$\cdots$O1^{ii}	0.74 (2)	2.14 (3)	2.8410 (16)	158 (2)
O5—H3$\cdots$O2^{iii}	0.81 (3)	2.09 (3)	2.8387 (15)	153 (2)
O5—H4$\cdots$O7	0.82 (2)	1.93 (2)	2.7460 (17)	176 (2)
O4—H5$\cdots$O7^{iv}	0.79 (3)	1.96 (3)	2.7354 (17)	169 (2)

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

All atoms, excluding H atoms, were refined anisotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1223). Services for accessing these data are described at the back of the journal.

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