Localization of Hydrogen Atoms by Neutron Profile Refinement of Vanadyl Sulphate Trihydrate, VOSO$_4$.3D$_2$O

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Abstract. Neutron powder data collected at 300 K with 1·909 Å radiation have been refined to give the D atom positions. VOSO$_4$.3D$_2$O has space group $P2_1/n$, with $Z = 4$. Crystal data from neutron diffraction data [X-ray diffraction data] are $a = 7·3972 (3)$ [7·387 (2)], $b = 7·4186 (3)$ [7·401 (2)], $c = 12·0756 (4)$ [12·046 (2)] Å, $\beta = 106·506 (3)$ [106·57 (3)]°, $V = 635·36 (8)$ [631·2 (1·1)] Å^3, $R_I = 0·128$ [$R_F = 0·0318$] for 649 [2117] observed reflections [λ(X-ray) $= 0·71069$ Å]. The hydrogen-bond scheme obtained previously from single-crystal X-ray diffraction has been improved. Two hydrogen bonds have been shown to be weak, and four to be normal. One water molecule is tetrahedral, two are trigonal.

Introduction. The present structure, VOSO$_4$.3D$_2$O, has been studied previously by single-crystal X-ray diffraction (Tachez & Théobald, 1980). In the last refinement, which was performed by least squares from diffractometer data, we concluded that three hydrogen atoms, H(21), H(22) and H(42), were not well located. The present study was undertaken to confirm the hydrogen-bond scheme proposed earlier.

A blue powder of VOSO$_4$.3D$_2$O was obtained by hydrating anhydrous α-VOSO$_4$ (Longo & Arnott, 1970) in a sealed glass tube (200 cm^3) with D$_2$O vapour pressure at 300 K. In fact the actual content of deuterated water molecules was not 100% but only 76% as indicated after structure refinement. The difference was due to the fact that the deuterated water was not 100% D$_2$O and also due to the isotopic exchange while handling samples. The powder material was placed in a 12 mm vanadium can.

The neutron diffraction experiment was performed on the D1A diffractometer of the Institut Laue–Langevin in Grenoble with the neutron wavelength 1·909 Å covering an effective 2θ range of 6 to 160° in steps of 0·05°. The scattering lengths used were those of *International Tables for X-ray Crystallography* (1974).

Rietveld's (1969) least-squares refinement program modified by Hewat (1973a,b) was used to refine 71 parameters with isotropic temperature factors to an R^* of 0·128.† The starting point was the X-ray structure (Tachez & Théobald, 1980).

No correction for preferred orientation or absorption was made. No attempt was made to use anisotropic thermal parameters since the quality of the data did not justify it.

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* R is defined as $\sum|I_o - (1/c)I_c|/\sum I_o$, where I_o and I_c are observed and calculated separated intensities for each Bragg peak.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36706 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters with e.s.d.'s in parentheses*

	x	y	z	B_{iso} (Å^2)
V*	0·5680 (1)	0·2831 (1)	−0·1253 (1)	0·99 (3)
S	0·229 (2)	0·358 (2)	−0·012 (1)	0·8 (2)
O(1)	0·444 (1)	0·4032 (9)	−0·2249 (7)	2·0 (2)
O(2)	0·760 (1)	0·103 (1)	0·0184 (7)	1·6 (2)
O(3)	0·440 (1)	0·041 (1)	−0·1715 (8)	2·5 (2)
O(4)	0·769 (1)	0·202 (1)	−0·2072 (8)	2·0 (2)
O(5)	0·760 (1)	0·458 (1)	−0·0348 (6)	1·6 (2)
O(6)	0·425 (1)	0·300 (1)	−0·0071 (7)	1·9 (2)
O(7)	0·158 (1)	0·2320 (9)	0·0624 (7)	1·9 (2)
O(8)	0·110 (1)	0·3582 (9)	−0·1306 (7)	2·4 (2)
D(21)	0·885 (1)	0·162 (1)	0·0510 (8)	3·0 (2)
D(22)	0·794 (1)	−0·008 (1)	−0·0185 (9)	2·8 (2)
D(31)	0·364 (2)	−0·016 (2)	−0·129 (1)	5·0 (3)
D(32)	0·407 (1)	−0·010 (1)	−0·2490 (9)	2·6 (2)
D(41)	0·726 (1)	0·226 (1)	−0·291 (1)	2·6 (2)
D(42)	0·887 (1)	0·255 (1)	−0·1807 (9)	2·9 (2)

* For the V atom, the atomic parameters are those of the X-ray method.

The site occupancy of the D atoms was refined to allow for the effect of D/H substitution. The cell parameters (*Abstract*) determined from profile analysis have very high accuracy (Hewat, 1973a). The final coordinates for the D atoms [also designated H(21), ..., H(42) elsewhere in this paper] are given in Table 1.

Discussion. The coordinates of the non-hydrogen atoms in the present investigation are in good agreement with those obtained by X-ray techniques. The description of the structure is therefore the same: two VO_6 octahedra share two neighbouring oxygen atoms with two SO_4 tetrahedra to build a dimer $[VO(H_2O)_3SO_4]_2$. The previous localization of D atoms by the X-ray single-crystal method was quite good except for D(21) which was supposed to be involved in a bifurcated hydrogen bond. D(21) is now shifted towards $O(7^i)$ to give a normal hydrogen bond. Table 2 gives interatomic distances and bond angles in the water molecules and the hydrogen bonds.

In a survey of water-molecule geometry in crystalline hydrates determined by neutron diffraction, Ferraris & Franchini-Angela (1972) found the average values 0.956 Å for the O—H length and 107.8° for the H—O—H angle. In the present study the averages are 0.97 (2) Å and 105 (2)°. Brown (1976) has, from a bond valence analysis of the repulsion between the O atoms in an OH···O bond, predicted a correlation between the O···H distance and the O—H···O angle. In this structure, there are two weak hydrogen bonds: $O(7^i)\cdots H(21)$ 2.05 (2) Å and $O(2^{ii})\cdots H(31)$ 1.94 (2) Å with O—H···O angles 158 and 168°. This first value but not the second is in good agreement with Brown's (1976) correlation. The four other O···H hydrogen bonds between 1.72 (1) and 1.81 (1) Å are stronger and their O—H···O angles are between 166 and 179° as predicted from Brown's paper. The hydrogen bond is much more bent when the O···H distance is longer.

The environment of the water molecule $H_2O(3)$ is trigonal [type *D* in Ferraris & Franchini-Angela's (1972) classification], *i.e.* the V—O bond is approxi-
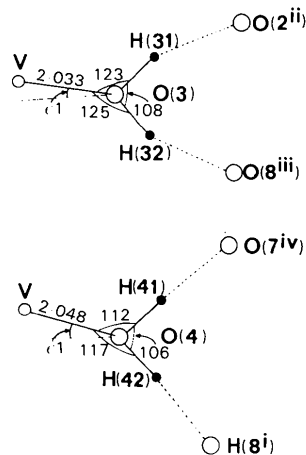

Fig. 1. The environment of the trigonal water molecules. (Distances in Å, angles in deg.)
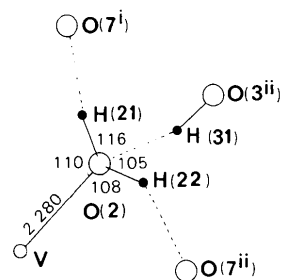

Fig. 2. The environment of the tetrahedral water molecule. (Distances in Å, angles in deg.)

mately along the bisector of the lone-pair orbitals of the water molecule. The environment of the water molecule $H_2O(4)$ is also trigonal but it belongs to type *J*, *i.e.* the V—O bonds are approximately along one lone-pair orbital of the water molecule. The values of angles ε_1 between V—O and the H_2O bisector are 26 and 48° (Fig. 1). The third water molecule $H_2O(2)$ is tetrahedral (Fig. 2), including the hydrogen atoms H(21) and H(22) and, in the directions of the lone pairs, atoms V and H(31); it belongs to class *H* according to Ferraris & Franchini-Angela (1972).

Table 2. *Geometric characteristics of water molecules and hydrogen bonds* (Å, °)

X-ray values are in square brackets.

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

1 2 3 4 5	d_{23}	d_{34}	∠234	d_{12}	d_{45}	∠123	∠345	d_{13}	d_{35}
O(7')···H(21)–O(2)–H(22)···O(7''')	1.00 (1) [0.81 (13)]	1.00 (1) [0.99 (10)]	102 (1) [114 (12)]	2.05 (2) [2.42 (15)]	1.81 (1) [1.88 (9)]	158 (1) [128 (14)]	168 (1) [149 (9)]	[2.996 (3)]	[2.778 (3)]
O(2'')···H(31)–O(3)–H(32)···O(8''')	0.95 (2) [0.86 (6)]	0.97 (1) [0.81 (5)]	108 (1) [106 (5)]	1.94 (2) [2.05 (6)]	1.73 (1) [1.92 (5)]	168 (1) [169 (5)]	166 (1) [158 (5)]	[2.904 (3)]	[2.687 (4)]
O(7'')···H(41)–O(4)–H(42)···O(8')	0.99 (1) [1.12 (5)]	0.93 (1) [0.89]	106 (1) [113]	1.72 (1) [1.60 (5)]	1.76 (1) [1.82]	178 (1) [170 (5)]	179 (1) [174]	[2.715 (3)]	[2.704 (4)]

References

Brown, I. D. (1976). *Acta Cryst.* A**32**, 24–31.

Ferraris, G. & Franchini-Angela, M. (1972). *Acta Cryst.* B**28**, 3572–3583.

Hewat, A. W. (1973*a*). Rutherford Report RRL 73/239. The Rietveld computer program for the profile refinement of neutron diffraction powder patterns modified for anisotropic thermal vibrations.

Hewat, A. W. (1973*b*). *J. Phys. C*, **6**, 2559–2572.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Longo, J. M. & Arnott, R. J. (1970). *J. Solid State Chem.* **1**, 394–398.

Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

Tachez, M. & Théobald, F. (1980). *Acta Cryst.* B**36**, 2873–2880.

Refinement of the Structure of Tellurium Phosphate Te₂O₃.HPO₄*

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Abstract. Te₂HPO₇, orthorhombic, $Pca2_1$, $a = 10.239$ (1), $b = 7.018$ (1), $c = 7.933$ (1) Å, $V = 570.1$ (1) Å³, $Z = 4$, $M_r = 399.2$, $D_c = 4.65$ g cm⁻³, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 105.2 cm⁻¹; data for 696 diffractometer-observed reflections $[I/\sigma(I) \geq 3.0]$, $R = 0.022$. The two Te atoms adopt trigonal-bipyramidal geometry [Te–O 1.903 (9)–2.183 (8) Å] with several secondary interactions [Te$\cdots$O 2.730 (10)–3.262 (8) Å], the shortest of which completes distorted square-based pyramidal geometry at Te(2).

Introduction. Several Te^{IV} oxy salts are reported to exist (Klein & Morel, 1885), including the nitrate Te₂O₄.HNO₃ (Swink & Carpenter, 1966), the sulphate Te₂O₃SO₄ (Johansson & Lindqvist, 1976; Hubková, Loub & Syneček, 1966) and the two phosphates Te₂O₃.HPO₄ (Mayer, 1975) and Te₄O₅(PO₄)₂ (Mayer & Pupp, 1977), whose structures are known. Reports of the perchlorate 2TeO₂.HClO₄ (Fichter & Schmid, 1916), the periodate 2TeO₂.HIO₄ (Montignie, 1945) and another phosphate 2TeO₂.HPO₄ (Mayer, 1975) do not include structural information. The structures of several aryl-substituted Te salts (Alcock & Harrison, 1982) all contain secondary bonds and it was decided to investigate the remaining unsubstituted salts. We have found that the reported preparations of the perchlorate and periodate give only crystals of tetragonal α-TeO₂ and orthotelluric acid respectively.

We repeated the reported preparation of 2TeO₂.H₃PO₄, isolating colourless platy crystals by dissolving TeO₂ in orthophosphoric acid at 383 K and allowing the solution to cool. The air-stable crystals were collected, washed with water and acetone and dried in air. On examination by single-crystal X-ray analysis, the crystals were found to be identical to those of the previously reported Te₂O₃.HPO₄. As this structure was based on Weissenberg data, refined isotropically to $R = 0.10$, we describe here a refinement to higher accuracy enabling us to discuss the primary and secondary bonding in more detail.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. The maximum 2θ was 50°, with a scan range of $\pm 1.0°$ (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, and the scan speed was 2–29° min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 100 reflections, and showed no significant changes during data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 696 observed reflections $[I/\sigma(I) \geq 3.0]$ were used in the refinement, and corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970). Systematic absences, 0*kl*, *l* $\neq 2n$; *h0l*, *h* $\neq 2n$; *h*00 (*h* $\neq 2n$), indicate space group $Pca2_1$, as in the previous report.

The positions of two Te atoms were located by direct methods using *MULTAN* 80 (Main, 1980) and a trial solution, after two cycles of isotropic refinement, gave $R = 0.182$. The remaining non-H atoms were located by successive difference Fourier syntheses and anisotropic least-squares refinements. An empirical weighting scheme was employed giving decreased weight to reflections with high F_{obs} and low sin θ. The final R

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*Secondary Bonding. 10. Part 9: Alcock & Harrison (1982).