Similarity with $(NH_4)_2H_3PO_4SO_4$ (*Averbuch-Pouchot*, 1981)

From the transformations

$$R = \begin{bmatrix} \frac{\bar{1}}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix} + \tau = \begin{bmatrix} 0 \\ 0 \\ \frac{1}{2} \end{bmatrix},$$

we derive the new fractional coordinates of the atoms and compare them with those in the P/S disordered structure (Table 3). We can see that small displacements are required to go from the disordered structure to the ordered one and that the ordering of XO_4 groups is reached by doubling the unit-cell volume. The title structure is then a superstructure of the disordered one. Baur (1981) gives for phosphate, sulfate and arsenate groups the following mean bond lengths: $\langle$P—O$\rangle$ = 1·537, $\langle$S—O$\rangle$ = 1·473, $\langle$As—O$\rangle$ = 1·682 Å. The differences between the mean X—O bond lengths of the two tetrahedral oxo ions $[\delta(X/Y) = |\langle X\text{—O}\rangle - \langle Y\text{—O}\rangle|]$ involved in each structure agree with the accepted ideas about possible order (disorder) in the two different tetrahedral groups: δ(P/S) = 0·06, δ(As/S) = 0·21 Å.

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Structure of Tetrapotassium Tetrametaphosphate Tetrahydrate

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Abstract. $K_4P_4O_{12}.4H_2O$, $M_r = 544{\cdot}35$, tetragonal, $I\bar{4}$, $a = 9{\cdot}061$ (3), $c = 10{\cdot}284$ (5) Å, $V = 844{\cdot}3$ Å^3, $Z = 2$, $D_x = 2{\cdot}141$ Mg m^{-3}, λ(Ag $K\alpha$) = 0·5608 Å, μ = 0·76 mm^{-1}, $F(000) = 544$, $T = 293$ K, final $R = 0{\cdot}030$ for 826 independent reflexions. P_4O_{12} ring anions are located around the $\bar{4}$ axis and form layers in planes $z = 0$ and 0·5. These layers are interconnected by K polyhedra and H bridges of the water molecules.

Introduction. The existence of two crystalline forms for potassium tetrametaphosphate tetrahydrate and of two forms for the anhydrous salt are reported in the chemical literature (Van Wazer, 1966). We recently described the chemical preparation and crystal structure of a triclinic dihydrate: $K_4P_4O_{12}.2H_2O$ (Averbuch-Pouchot & Durif, 1985). The present work deals with the crystal structure of the tetragonal tetrahydrate.

Experimental. As described in a previous paper (Averbuch-Pouchot & Durif, 1985), $K_4P_4O_{12}.2H_2O$ is easily prepared by adding freshly prepared tetrametaphosphoric acid to an iced solution of $KHCO_3$ or K_2CO_3. To the resulting solution is then added a large excess of ethyl alcohol to precipitate the tetrametaphosphate. The precipitate so obtained is very often a gel, crystallizing slowly and producing $K_4P_4O_{12}.2H_2O$ crystals. If some pellets of KOH are added to a freshly prepared gel, the speed of crystallization is increased and the resulting crystals are large pseudo-hexagonal prisms of $K_4P_4O_{12}.4H_2O$.

Crystal size: 0·40 × 0·40 × 0·40 mm; D_m not measured; Philips PW 1100 diffractometer; graphite monochromator; systematic absences: $h + k + l = 2n$; 15 reflexions ($10 < \theta < 13°$) for refining the unit cell; ω scan; scan speed: 0·02° s^{-1}; scan width: 1·20°; total background measuring time: 20 s; intensity and orientation reflexions: 008 and 00$\bar{8}$ (no significant variation in intensity); θ range: 3–30°; 1212 reflexions measured; $H_{max} = 16$, $L_{max} = 18$; Lorentz–polarization correction; no absorption correction; classical methods for structure determination: Patterson function and successive Fourier syntheses; H atoms located from

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difference-Fourier synthesis; anisotropic full-matrix least-squares refinement on F for non-hydrogen atoms, isotropic for H atoms; unit weights; 1111 independent reflexions; final refinements with a set of 826 reflexions corresponding to the rejection of 281 reflexions with $F_o < 3\sigma$ and 4 very strong ones poorly measured; extinction refined: $g = 0{\cdot}5 \times 10^{-6}$ (Stout & Jensen, 1968); final $R = 0{\cdot}030$ ($wR = 0{\cdot}035$), $S = 0{\cdot}533$; for the total set of 1111 independent reflexions $R = 0{\cdot}038$, $\Delta\rho_{\max} = 0{\cdot}3$ e Å^{-3}, $(\Delta/\sigma)_{\max} < 0{\cdot}02$ except for H(1) (0·07) and H(2) (0·26);* scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations.

Discussion. Fig. 1, a projection along **c**, depicts the location of the ring anions in the atomic arrangement while Fig. 2 is a projection along **b** of the whole structure. Table 1 reports the final atomic coordinates.

The P_4O_{12} groups are located around the $\bar{4}$ axis. Table 2 reports their main geometrical features, showing the four P atoms and the four bonding O atoms [O(L)] to be almost coplanar. It is worth noting that K atoms, water molecules and the two external O atoms of the rings are all located in planes $z \sim \pm 0{\cdot}13$. As shown in Fig. 2, connexions between these layers are provided by the K polyhedra and the hydrogen bonds. Main interatomic distances in the K polyhedron are reported in Table 2. Within a range limited to K—O < 3·5 Å this polyhedron is built up by four O atoms and three water molecules. Characteristics of the hydrogen-bond scheme are given in Table 2. It should be noted that the external oxygen O(E1) acts twice as an acceptor.

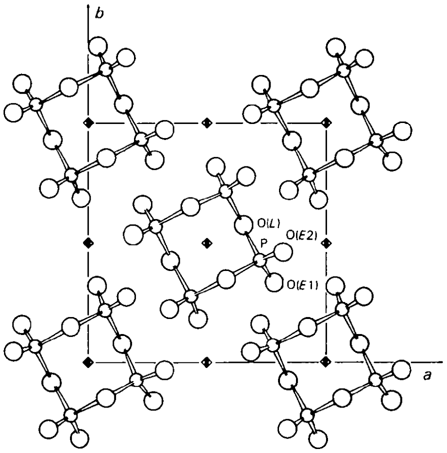

Fig. 1. Projection along **c** of the P_4O_{12} ring anions. Water molecules and K atoms are not represented.

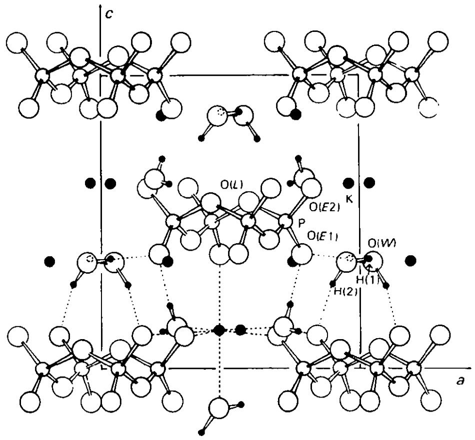

Fig. 2. Projection along **b** of the atomic arrangement of $K_4P_4O_{12}.4H_2O$.

Table 1. *Final atomic coordinates for* $K_4P_4O_{12}.4H_2O$ *and isotropic thermal parameters* (Å^2), *with e.s.d.'s in parentheses*

For non-H atoms $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq} or B_{iso}
K	0·45927 (9)	0·2444 (1)	0·13320 (8)	2·18 (2)
P	0·07129 (8)	0·21842 (8)	−0·0005 (1)	1·27 (1)
O(E1)	0·8406 (3)	0·7240 (3)	0·1108 (3)	2·01 (6)
O(E2)	0·5367 (3)	0·8180 (3)	0·3895 (3)	1·95 (6)
O(L)	0·9243 (3)	0·1497 (3)	0·0625 (2)	1·49 (5)
O(W)	0·0488 (4)	0·2078 (4)	0·3613 (3)	2·93 (8)
H(1)	0·966 (7)	0·263 (7)	0·372 (6)	5·0 (2·0)
H(2)	0·106 (9)	0·235 (10)	0·285 (8)	9·0 (2·0)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in* $K_4P_4O_{12}.4H_2O$

The PO_4 tetrahedron

P	O(E1)	O(E2)	O(L)	O(L)
O(E1)	1·490 (4)	2·563 (5)	2·469 (5)	2·546 (5)
O(E2)	119·2 (2)	1·481 (4)	2·557 (5)	2·472 (5)
O(L)	105·6 (2)	111·7 (2)	1·607 (4)	2·505 (5)
O(L)	110·5 (2)	106·3 (2)	102·4 (2)	1·607 (4)
	P—O(L)—P	132·6 (2)	P—P	2·944 (2)
	P—P—P	90·00 (3)		

Equation of the average plane of the ring: $z = 0$. Distances from plane: P ±0·006; O(L) ±0·046 Å.

The KO_7 polyhedron

K—O(E1)	2·742 (4)	K—O(W)	2·832 (5)
K—O(E2)	2·698 (4)	K—O(W)	2·930 (5)
K—O(E2)	2·860 (4)	K—O(W)	3·146 (5)
K—O(E2)	2·769 (4)		

The hydrogen bonds

	O(W)—H	H···O	O(W)—O	∠O(W)—H···O	∠H—O(W)—H
O(W)—H(1)···O(E1)	0·91 (10)	1·86 (10)	2·764 (6)	169 (9)	113 (9)
O(W)—H(2)···O(E1)	0·97 (14)	1·89 (14)	2·835 (7)	162 (11)	

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42404 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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X-ray Structure Determination of Divanadium Hydride, β_1-V_2H, and Divanadium Deuteride, β-V_2D

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Abstract. β_1-V_2H: $M_r = 102{\cdot}89$, tetragonal, $I4_1/amd$, $a = 6{\cdot}0349\,(4)$, $c = 6{\cdot}8716\,(3)$ Å, $V = 250{\cdot}3$ Å^3, $D_x = 5{\cdot}46$ Mg m^{-3}, $Z = 8$, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 13{\cdot}65$ mm^{-1}, $F(000) = 376{\cdot}0$, room temperature, final $R = 0{\cdot}031$ for 154 independent reflections; β-V_2D: $M_r = 103{\cdot}9$, monoclinic, Cm, $a = 4{\cdot}4554\,(7)$, $b = 3{\cdot}0090\,(3)$, $c = 4{\cdot}4719\,(7)$ Å, $\beta = 95{\cdot}30\,(1)°$, $V = 59{\cdot}70\,(1)$ Å^3, $D_x = 5{\cdot}78$ Mg m^{-3}, $Z = 2$, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 14{\cdot}31$ mm^{-1}, $F(000) = 94{\cdot}0$, room temperature, final $R = 0{\cdot}024$ got 598 independent reflections. The crystal structures of β_1-V_2H and β-V_2D have been studied using a four-circle diffractometer with Mo $K\alpha$ radiation, and refined by the full-matrix least-squares method. The specimens examined were grown under tensile stresses. The positional and thermal parameters of V atoms in β_1-V_2H and β-V_2D are found to be hydrogen-isotope dependent and reflect directly the respective ordered arrangements of the H and D atoms which are located in the different types of octahedral interstices of the metal lattices.

Introduction. The vanadium–hydrogen(deuterium) system has been the subject of extensive studies because of its significant isotope effects on equilibrium phase diagrams (Asano & Hirabayashi, 1973, 1977; Schober & Wenzel, 1978; Moss, 1983), diffusion constant (Völkl & Alefeld, 1978; Bowman, Attalla & Craft, 1983) and crystal structures (Somenkov & Shil'shtein, 1980; Asano & Hirabayashi, 1979, 1981).

The atomic arrangements of hydrogen in β_1-V_2H and of deuterium in β-V_2D have been studied by several workers by X-ray, neutron and electron diffraction. The structural models proposed so far for these two compounds are summarized in Table 1. In all the models, the H(D) atoms occupy orderly specific octahedral interstices in the fundamental body-centered lattice of the V atoms. The metal lattice proposed is either monoclinic or tetragonal with the axial ratio $c_0/a_0 \simeq 1{\cdot}1$. For the monoclinic model, the space groups $C2$, Cm and $C2/m$ are assumed for the hydride, and Cm is chosen for the deuteride. The tetragonal model of space group $I4_1/amd$ is presented alternatively for the deuteride. The monoclinic and tetragonal models are illustrated in Fig. 1: in the monoclinic model (*a*), the rows of the H(D) atoms in the base-centered positions of the metal lattice are parallel to those in the edge-centered positions, while they are normal to each other in the tetragonal model (*b*). On the other hand, some fraction of H(D) atoms in β_1-V_2H (Wanagel, Sass & Batterman, 1972) and in β-V_2D (Westlake, Mueller & Knott, 1973) were suggested to occupy tetrahedral sites surrounding the H(D) atom at an octahedral site.

A recent study by single-crystal neutron diffraction (Kajitani & Hirabayashi, 1985) indicates that the crystal structure of β_1-V_2H differs from that of β-V_2D in the arrangement of H(D) atoms, and corresponds to the model of $I4_1/amd$. In the neutron diffraction study, however, vanadium atoms cannot be seen since its

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