

Hydrogen Uranyl Phosphate Tetrahydrate, a Hydrogen Ion Solid Electrolyte*

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Abstract. $\text{H}_2\text{O}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$, $P4/ncc$, $a = 6.995$ (2), $c = 17.491$ (4) Å, $Z = 4$, $V = 855.84$ Å³, $D_c = 3.399$ g cm⁻³. The structure has been refined using 695 Mo $K\alpha$ ($\lambda = 0.710688$ Å, $\mu = 166$ cm⁻¹) intensities to $R = 0.025$. The two-dimensional network of hydrogen bonds serves as the path for H^+ ion conduction in this material.

Introduction. Recent electrochemical studies by Shilton & Howe (1977) have shown $\text{H}_2\text{O}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP), to be one of the few candidate materials exhibiting H^+ ion conduction. Our preliminary structural study (Morosin, 1978) supported their suggestion of the importance of the hydrogen bonding in HUP and the probable mechanism for H^+ ion conductivity. Details of our structure refinement are given in this paper.

HUP belongs to a class of structurally similar, layered compounds; this structure type was first described by Beintema (1938) and subsequently various members were studied in more detail by others (Ross & Evans, 1964; Ross, Evans & Appleman, 1964; Nuffield & Milne, 1953; Weigel & Hoffman, 1976; Botto, Baran & Aymonino, 1976). Single crystals of HUP may be obtained by slow diffusion of an aqueous $\text{UO}_2(\text{NO}_3)_2$ solution into one of H_3PO_4 . Intensities were measured on a thin slab ($0.32 \times 0.32 \times 0.04$ mm) bound by $\{110\}$ and $\{001\}$ using the θ - 2θ scan technique on one quadrant to $62^\circ 2\theta$ for Mo $K\alpha$. An automated Picker diffractometer with an E & A full circle orienter was used with a scintillation detector employing pulse-height discrimination. Cell dimensions given above were obtained from high 2θ values using Mo $K\alpha$ radiation. Absorption corrections (values varied from 1.94 to 34.8) were applied and symmetry-related values were averaged, yielding 695 intensities. Of these, $I < 3\sigma$ in 298 cases, where $\sigma = [1/n(N_{sc} + K^2N_b)]^{1/2}$ and N_{sc} , N_b , K , and n are the total scan count, background counts, the time ratio of the scan to background and the number of equivalent reflections; such $hk\ell$'s were considered as 'less-thans' and included in least-squares refinement whenever $F_o > F_c$. The function $\sum |w(F_o - F_c)|^2$ with $w = 1/\sigma^2$ was mini-

mized. Structure factors were calculated using scattering factors computed from Hartree-Fock wave functions (Cromer & Mann, 1968) and a dispersion correction for U of -8.0 . Analysis of the Patterson Fourier synthesis and the heavy-atom method yielded the structural model independent of previous results.

The origin selected (Fig. 1) is at $1, \frac{1}{4}, -\frac{1}{4}, 0$ from the $\bar{4}$ axis. Note that in this space group, the U, uranyl O and P atoms do not contribute to reflections with l odd. A residual index, R , on observed reflections of 0.087 is obtained ignoring the phosphate and water O atoms and of 0.052 ignoring the water molecules. The latter (0.052) difference Fourier synthesis contains two different possible water position sites with an electron density ratio of 2:3. The position corresponding to the lower-valued peak (0.666, 0.026, 0.188) may be forced to refine to $R = 0.033$, though the thermal parameters of the phosphate O will then not properly converge. Bond lengths and separations are all reasonable. This peak, however, is the ghost resulting from the true peak misplaced by $c/2$ using one of the symmetry operations $\frac{1}{2} - x, y, \frac{1}{2} + z$ of this space group. Convergence with the correct peak is rapid with final shifts to standard deviation ratios being less than 0.05. The resulting thermal parameter for the water O atom is about 2.5 times larger than those for the other O atoms. No significant shift in the final positional parameters for any atom is obtained when the 'less-thans' criteria is relaxed from 3σ to 1σ in order to increase the number of l odd reflections contributing to the refinement; this increases the number of contributing reflections from 477 to 646. The H-atom positions were not clearly resolved on this final difference syntheses and were thus not included in the calculations. The largest negative peaks ($-2.3 \text{ e } \text{Å}^{-3}$) on this map are about the U atom along the UO_2 axis while the largest positive peak (1.5

Table 1. Positional parameters for HUP

	x	y	z
U	$\frac{1}{4}$	$\frac{1}{4}$	0.04935 (4)
P	$\frac{3}{4}$	$\frac{1}{4}$	0
O(1)	$\frac{1}{4}$	$\frac{1}{4}$	0.1514 (8)
O(2)	$\frac{1}{4}$	$\frac{1}{4}$	-0.0507 (8)
O(3)	0.578 (1)	0.286 (1)	0.0509 (4)
O(4)	0.837 (2)	0.020 (2)	0.1891 (6)

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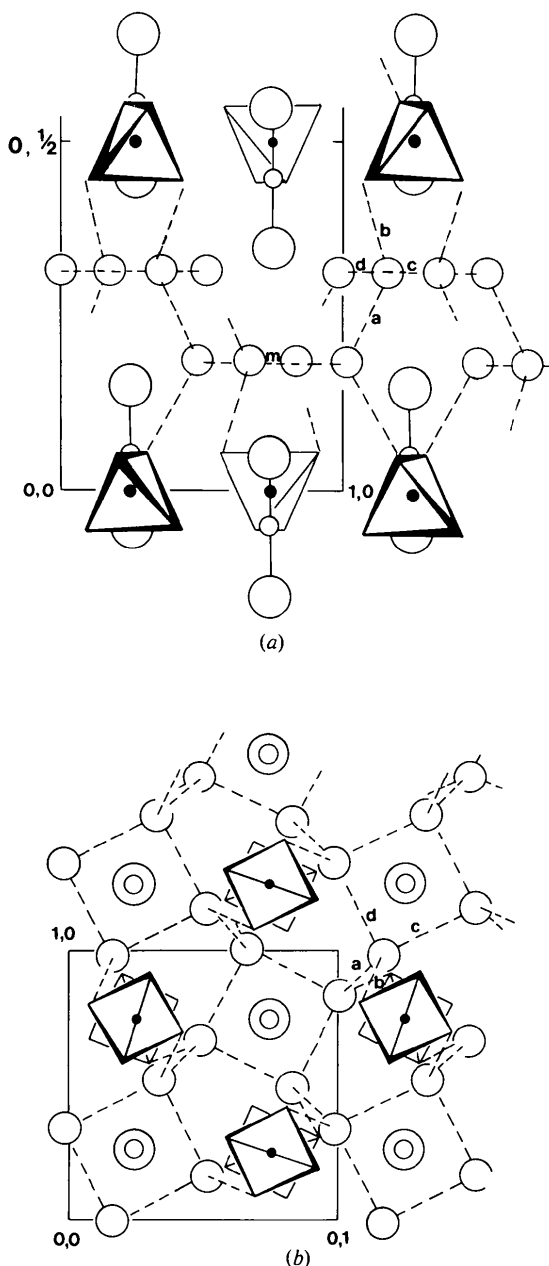


Fig. 1. Projections of the HUP structure along (a) [100], and (b) [001]. The water molecules of the network about $z = \frac{3}{4}$ have been omitted for clarity. The large open circles designate the uranyl oxygen, medium circles the water molecules, small open circles U and small, solid circles P. Oxygens of PO_4 are at the vertices of the tetrahedra. The values of the O—O separations for the hydrogen bonds (dashed lines) are (a) 2.56 (2), (b) 2.83 (1), (c) equal to (d) by symmetry 2.81 (2) Å with angles (ab) 116.2 (6)°, (ac) 121.7 (6)°, (ad) 99.8 (6)°, (bc) 113.9 (5)°, (bd) 109.3 (5)° and (cd) 90.0°. The differences in the hydrogen-bond lengths may result from a higher statistical occupancy factor for type (a) compared with (b) or (c) sites. In HUP there is an empty octahedral site, labeled *m*, which is found to contain smaller ions in some structurally related materials.

$e \text{ \AA}^{-3}$) is at the P position with ripples as large as $\pm 0.8 e \text{ \AA}^{-3}$ elsewhere. A final residual index on observed reflections of 0.025 was obtained with positional parameters given in Table 1 (R is 0.033 including 'less-than' reflections).^{*} The XRAY 76 system (Stewart, 1976) was employed for calculations.

Discussion. This structure consists of two-dimensional networks of water molecules, which also contain the remaining H^+ ion, alternating with layers of UO_2^{2+} and PO_4^{3-} ions; these networks are located about $z = \frac{1}{4}$ and $z = \frac{3}{4}$ (Fig. 1). The UO_2^{2+} ion is linear by symmetry with U—O(1) and U—O(2) bond distances of 1.78 (1) and 1.75 (1) Å, respectively, while the slightly distorted [108.2 (4) and 110.1 (4)° angles formed with O with same and different z parameters, respectively] PO_4^{3-} ion involves a 1.519 (8) Å P—O(3) bond distance. The four equatorial O(3) atoms about UO_2^{2+} are at 2.307 (8) Å from U on a plane 0.027 (8) Å displaced toward O(1). The nearest O contacts for O(1) are four O(3) atoms at 2.90 (1) Å and four O(4) atoms at 3.37 (1) Å and for O(2) are four O(3) atoms at 2.91 (1) Å and four O(4) atoms at 3.13 (2) Å. The hydrogen-bond network connects the water molecules as well as the PO_4^{3-} ions in the structure; values of O—O separations and angles are given in Fig. 1. In these two-dimensional networks, each water molecule participates in four hydrogen bonds; thus, there are more hydrogen-bond sites available than H^+ ions (for every four oxygens, there are nine H^+ ions to be distributed over ten hydrogen-bond sites). In addition, the H^+ ion is probably situated closer to one of the two water O atoms in six of these hydrogen-bond sites. The exact distribution of these statistically disordered H atoms will require further studies employing tools other than X-ray diffraction.

Details on the migration of the H^+ ions in the network have been detailed elsewhere (Morosin, 1978; Childs, Halstead, Howe & Shilton, 1978).

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33810 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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β -Uranyl Sulphate and Uranyl Selenate

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Abstract. β - UO_2SO_4 , monoclinic, $P2_1/c$, $a = 6.760$ (1), $b = 5.711$ (1), $c = 12.824$ (4) Å, $\beta = 102.91$ (2)°, $V = 482.6$ Å³, $Z = 4$, $D_c = 5.04$ g cm⁻³. α - UO_2SeO_4 , monoclinic, $P2_1/c$, $a = 6.909$ (1), $b = 5.525$ (1), $c = 13.318$ (3) Å, $\beta = 103.79$ (2)°, $V = 493.7$ Å³, $Z = 4$, $D_c = 5.569$ g cm⁻³. β - UO_2SeO_4 , monoclinic, $P2_1/c$, $a = 6.979$ (1), $b = 5.795$ (1), $c = 13.235$ (2) Å, $\beta = 103.71$ (2)°, $V = 520.0$ Å³, $Z = 4$, $D_c = 5.279$ g cm⁻³. The structures of the isostructural title compounds have been solved from X-ray and neutron diffraction powder data. U atoms are coordinated by pentagonal bipyramids of O atoms. Remarkably, a uranyl O atom of one bipyramid belongs to the pentagonal base plane of the next.

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Table 1. Coordinates and thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
(a) For β - UO_2SO_4				
U	0.315 (1)	0.744 (1)	0.658 (1)	1.3 (2)
S	0.209 (4)	0.454 (5)	0.888 (2)	2.7 (7)
O(1)	0.612 (2)	0.789 (2)	0.592 (1)	1.5 (2)
O(2)	0.220 (2)	0.954 (2)	0.502 (1)	1.5 (2)
O(3)	-0.028 (2)	0.816 (2)	0.643 (1)	1.5 (2)
O(4)	0.241 (2)	0.632 (2)	0.822 (1)	1.5 (2)
O(5)	0.604 (2)	0.514 (3)	0.774 (1)	1.5 (2)
O(6)	0.254 (2)	0.478 (2)	0.595 (1)	1.5 (2)
(b) For α - UO_2SeO_4				
U	0.338 (2)	0.709 (2)	0.648 (1)	1.2 (4)
Se	0.201 (2)	0.440 (3)	0.887 (1)	1.3 (5)
O(1)	0.650 (3)	0.711 (3)	0.613 (1)	1.4 (3)
O(2)	0.300 (2)	0.878 (4)	0.484 (1)	1.4 (3)
O(3)	0.016 (3)	0.852 (4)	0.600 (1)	1.4 (3)
O(4)	0.175 (2)	0.598 (4)	0.781 (1)	1.4 (3)
O(5)	0.581 (2)	0.484 (4)	0.784 (1)	1.4 (3)
O(6)	0.266 (2)	0.422 (4)	0.590 (1)	1.4 (3)

Introduction. The structure determinations were undertaken in connection with thermochemical investigations on uranyl salts of oxyacids containing Group VI elements (Brandenburg, 1978; Cordfunke & Ouweltjes, 1977).

β - UO_2SO_4

Anhydrous β - UO_2SO_4 was prepared by dehydration of $\text{UO}_2\text{SO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (Cordfunke, 1969) in air at 500°C. Analysis gave U: 65.07% (calc. 65.02%). Neutron powder data were collected at the HFR in Petten [0.02

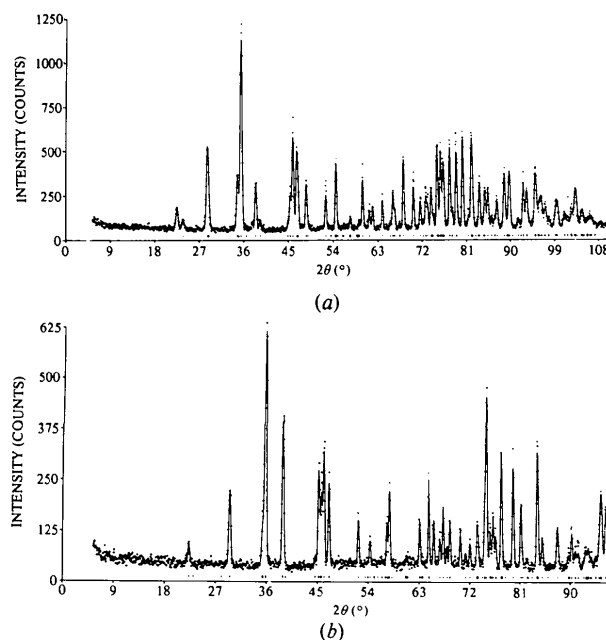


Fig. 1. Observed and calculated neutron powder pattern of (a) β - UO_2SO_4 , (b) α - UO_2SeO_4 . Full line: calculated profile; dots: measurements.