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The Room-Temperature Structure of $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ by Powder Neutron Diffraction

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Abstract. $M_r = 491.1$, space group $P4/ncc$, $a = 7.1615$ (1), $c = 17.6390$ (2) Å, $Z = 4$. The structure was determined from a powder neutron diffraction study at 305 K. The profile resulting from 265 reflections was refined to an R_{wp} of 6.51%. The study locates the H atoms and demonstrates that the hydrogen disorder is confined to the hydrogen bond between O atoms within the squares of water molecules.

Introduction. The layered hydrates $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP) and $\text{HUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (HUAs) exhibit high proton mobility, as shown by conductivity studies (Shilton & Howe, 1977; Howe & Shilton, 1979, 1980), and measurements by pulsed proton NMR (Childs, Halstead, Howe & Shilton, 1978; Gordon, Strange & Halstead, 1979).

Morosin (1978) performed a single-crystal X-ray diffraction study on HUP at room temperature, in which the positions of all the atoms except the hydrogens were located. HUP crystallizes in space group $P4/ncc$ with $Z = 4$ and $a = 6.995$ (2), $c = 17.491$ (4) Å. The structure consists of two-dimensional networks of water molecules, grouped into squares also containing the remaining H^+ ion, which

alternate with layers of UO_2^{2+} and PO_4^{3-} ions. These water-molecule networks are located about $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The UO_2^{2+} ion is linear by symmetry along the c axis and the U atom is coordinated equatorially by four coplanar O atoms of four different PO_4^{3-} groups. The hydrogen-bond network connects the water molecules both to each other and also to the PO_4^{3-} ions. In each two-dimensional water network each water molecule participates in four hydrogen bonds, so for every four oxygens there are nine hydrogens to be distributed over ten sites.

In an earlier paper (Bernard, Fitch, Howe, Wright & Fender, 1981) we gave a preliminary report of the hydrogen distribution, deduced from a powder neutron diffraction study on deuterated $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ (DUAs). The average scattering per unit cell was described in terms of the presence of two dimeric water species, H_4O_2 dimers and H_5O_2^+ ions, which were disordered and whose dynamic interchange provides a mechanism for hydrogen mobility in this compound (Bernard, Fitch, Wright, Fender & Howe, 1981). As the powder diffraction data appeared insufficient to resolve the individual atomic and thermal parameters associated with these two species, we had hoped to

acquire extra data from a single-crystal neutron diffraction study. However, the crystals of HUP which we examined, although large enough for a neutron study, showed such poor peak profiles that we could not perform an accurate single-crystal study. Given the layer-like structure of HUP, and hence the probability of stacking faults normal to the c direction, single crystals may be difficult or impossible to grow to a size or quality acceptable for the refinement of separate H_4O_2 and H_5O_2^+ units. We report fully in this paper, therefore, the quantitative structural information derived from the powder neutron diffraction study.

Experimental. A sample, 8.61 g of $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$, was prepared by Dr M. G. Shilton and sealed in a thin-walled vanadium sample can. Neutron powder diffraction studies were performed at 305 K on the high-resolution diffractometer D1A at the high-flux reactor at ILL (Grenoble) at a wavelength of 1.9094 Å. Diffraction data were collected in steps of 0.05° over an angular range from 6 to 155° in 2θ . The scan took about 20 h.

The diffraction pattern was analysed by the method of profile analysis (Rietveld, 1969), following the procedure described elsewhere (Fitch, Fender & Wright, 1982). The scattering lengths used were $U = 8.50$, $As = 6.40$, $O = 5.80$, $D = 6.67$ fm (Bacon, 1975).

The structure of DUAs at 305 K was refined in space group $P4/ncc$ with the origin at $\bar{1}$, using the atomic parameters obtained from the HUP single-crystal study (Morosin, 1978) as starting parameters for the heavy atoms. The occupancy of the available hydrogen-bond sites was as reported previously (Bernard, Fitch, Howe, Wright & Fender, 1981). The in-square hydrogen bonds [H(1)] are $\frac{3}{4}$ occupied with 12 H atoms statistically distributed over the 16 available positions in the unit cell. The hydrogen atoms [H(2)] directed towards the oxygen of an AsO_4^{3-} group

are bonded to the O atom of a water molecule and are fully occupied with 16 H atoms per unit cell. The remaining eight H atoms in the unit cell [H(3)] are in the inter-square linking position and are associated with a single maximum in scattering density situated midway between the two O atoms of two water molecules in neighbouring squares. This site is at the special crystallographic position $8(f)$ ($\bar{x}, x, \frac{1}{4}$) which lies on a twofold axis of symmetry.

Thus the final refinement, model (a), involved a total of 52 atomic parameters, the scale factor and the scattering length of deuterium, two lattice parameters, three half-width parameters, the zero point, asymmetry and preferred orientation parameters to correct for a small amount of alignment of the plate-like crystals normal to [001]. There were 265 reflections. The final R factors were $R_I = 3.88$, $R_{wp} = 6.22$, $R_p = 7.05$, $R_E = 3.58\%$. The final parameters are shown in Table 1. Important interatomic distances are in Table 2. The observed, calculated and difference profiles are in Fig. 1* and the structure is shown in Fig. 2.

In a second refinement, model (b), involving an extra four atomic parameters, the linking hydrogens H(3) were allowed to occupy the general position $16(g)$ (x, y, z), *i.e.* with half-occupied equivalent sites on either side of the twofold symmetry axis. The R factors were $R_I = 3.94$, $R_{wp} = 6.19$, $R_p = 7.03\%$, but the estimated standard deviations (e.s.d.'s) on the atomic coordinates and thermal parameters of H(3) increased by factors of 3 and 2 respectively. The other atoms in the structure did not change position by more than one e.s.d., except for O(4) to which H(3) is directly linked. The bond distances (Table 2) agree to within a single e.s.d. with

* A table giving the numbered intensity of each measured point on the profile, as a function of θ , has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38134 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final parameters for $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ at 305 K in space group $P4/ncc$ (origin at $\bar{1}$), $a = 7.1615$ (1), $c = 17.6390$ (2) Å

The anisotropic temperature factor has the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The parameters are in Å². E.s.d.'s are in parentheses.

| | Point | | | | | | | | | | |
|------|----------|-----------|---------------|---------------|---------------|----------|----------|----------|-----------|----------|----------|
| | Position | symmetry | x | y | z | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
| U | 4(c) | 4 | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.0527 (1) | 0.62 (6) | 0.62 (6) | 1.0 (1) | 0 | 0 | 0 |
| As | 4(b) | $\bar{4}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0 | 0.35 (6) | 0.35 (6) | 1.7 (1) | 0 | 0 | 0 |
| O(1) | 4(c) | 4 | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.1545 (2) | 1.86 (8) | 1.86 (8) | 1.42 (2) | 0 | 0 | 0 |
| O(2) | 4(c) | 4 | $\frac{1}{4}$ | $\frac{1}{4}$ | -0.0482 (2) | 2.04 (9) | 2.04 (9) | 1.2 (2) | 0 | 0 | 0 |
| O(3) | 16(g) | 1 | 0.5681 (2) | 0.2048 (2) | 0.0573 (1) | 0.56 (5) | 1.48 (5) | 2.07 (8) | -0.02 (4) | 0.41 (7) | 0.47 (5) |
| O(4) | 16(g) | 1 | 0.1476 (5) | 0.9977 (5) | 0.3095 (2) | 5.4 (2) | 9.8 (3) | 2.6 (2) | -2.9 (1) | 0.8 (1) | 2.3 (2) |
| H(1) | 16(g)* | 1 | 0.3037 (9) | 0.0404 (6) | 0.3112 (2) | 15.3 (3) | 7.6 (2) | 2.7 (2) | 5.3 (2) | 0.9 (2) | 0.9 (2) |
| H(2) | 16(g) | 1 | 0.5757 (3) | 0.1283 (2) | 0.3556 (2) | 5.7 (1) | 3.4 (1) | 3.0 (1) | 1.2 (1) | -0.2 (1) | 0.2 (1) |
| H(3) | 8(f) | 2 | 0.4057 (3) | -0.4057 (3) | $\frac{1}{4}$ | 6.3 (1) | 6.3 (1) | 10.0 (4) | 1.8 (2) | -3.8 (2) | -3.8 (2) |

* $\frac{3}{4}$ occupied.

those from model (a) for the uranyl and arsenate groups.

Table 2. Bond distances (Å) and angles (°) for $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ at 305 K for two different models

In model (a) the linking hydrogen H(3) is at $8(f)$ ($\bar{x}, x, \frac{1}{2}$). In model (b) H(3) is in the general crystallographic position $16(g)$ (x, y, z) with $x = 0.3847$ (11), $y = 0.5710$ (11), $z = 0.2640$ (7). E.s.d.'s are in parentheses.

| | Model (a) | Model (b) | Comment |
|--------------------|------------|------------|------------------------------|
| (1) Uranyl ion | | | |
| U—O(1) | 1.796 (3) | 1.794 (3) | |
| U—O(2) | 1.781 (4) | 1.782 (4) | |
| U—O(3) | 2.303 (1) | 2.304 (1) | |
| O(1)—U—O(2) | 180 | 180 | |
| O(1)—U—O(3) | 88.00 (6) | 88.00 (6) | |
| (2) Arsenate ion | | | |
| As—O(3) | 1.680 (1) | 1.680 (1) | |
| O(3)—As—O(3) | 106.00 (7) | 105.93 (7) | $z_1 = z_2$ |
| O(3)—As—O(3) | 111.23 (6) | 111.27 (6) | $z_1 = -z_2$ |
| U—O(3)—As | 136.0 (1) | 136.0 (1) | |
| (3) Water molecule | | | |
| O(4)—H(1) | 1.159 (7) | 1.145 (8) | |
| O(4)—H(2) | 0.979 (4) | 0.984 (5) | |
| O(4)—H(3) | 1.297 (4)* | 0.99 (1) | |
| O(4)—O(4) | 2.758 (5) | 2.751 (5) | |
| O(4)—O(4) | 2.565 (5) | 2.576 (5) | side of square link distance |
| H(1)—O(4) | 1.617 (7) | 1.624 (8) | |
| H(2)—O(3) | 1.845 (3) | 1.839 (3) | |
| H(3)—O(4) | 1.297 (4)* | 1.77 (1) | |
| O(4)—O(3) | 2.820 (4) | 2.821 (4) | |
| H(1)—O(4)—H(2) | 104.9 (4) | 105.5 (4) | |
| H(1)—O(4)—H(3) | 116.0 (3) | 109.5 (6) | |
| H(2)—O(4)—H(3) | 111.1 (3) | 108.9 (5) | |
| O(4)—H(1)—O(4) | 166.7 (4) | 166.6 (4) | |
| O(3)—H(2)—O(4) | 174.3 (3) | 174.7 (3) | |
| O(4)—H(3)—O(4) | 162.6 (3) | 162.0 (8) | |

* Related by symmetry in model (a).

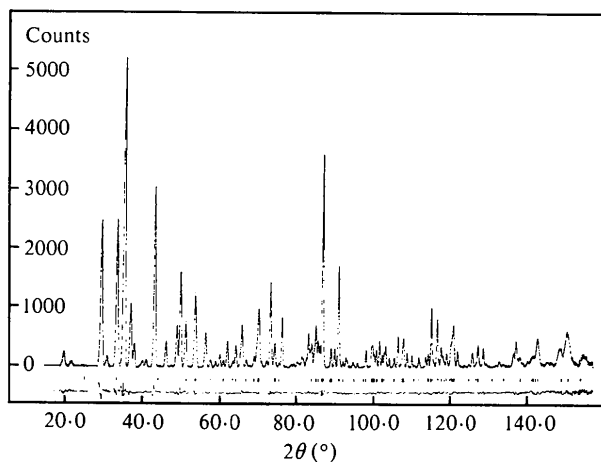


Fig. 1. Observed (points), calculated (full curve) and difference profiles for $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ at 305 K, with reflection positions.

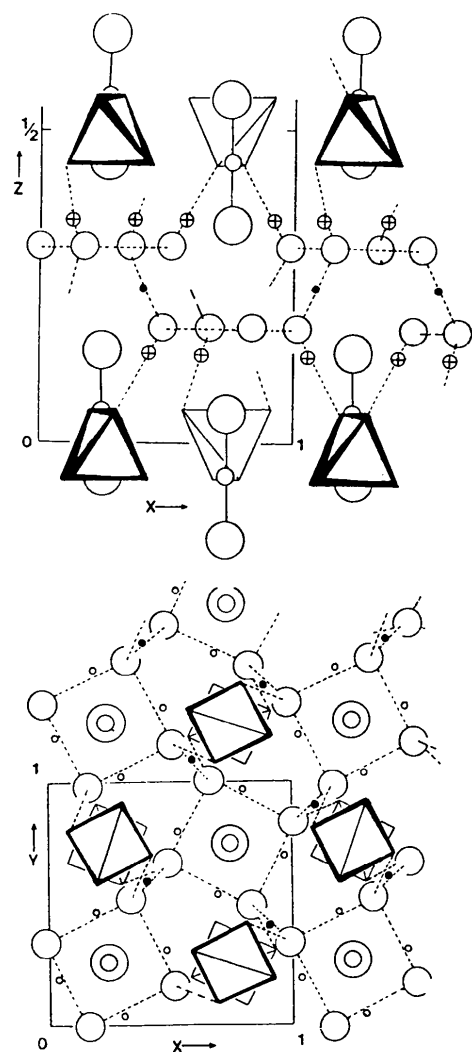


Fig. 2. Projection of the structure of $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ at 305 K along (top) [010] [H(1) hydrogens not shown] and (bottom) [001] [H(2) hydrogens not shown]. Large open circles, uranyl oxygens; medium open circles, water oxygens; tetrahedra, arsenate groups; smaller open circles, uranium; small black circles, H(3) hydrogens; smallest open circles, H(1) hydrogens; crossed circles, H(2) hydrogens.

Discussion. The refinements indicated that the degree of deuteration of the DUAs sample was better than 98% and that the arrangement of the non-hydrogen atoms is essentially identical to that found in HUP (Morosin, 1978). The U—O bond distances and the geometry of the phosphate or arsenate group are very similar in the two compounds, although the As—O(3) bond distance is longer than P—O(3) by 0.161 (8) Å which is very close to the difference of 0.165 Å which could be expected from ionic-radius considerations [As 0.335 Å, P 0.17 Å (Shannon & Prewitt, 1969)]. O—O hydrogen-bonded distances are little altered although the in-square O(4)—O(4) separation is decreased by

0.05 (2) Å in DUAs as a result of the rotation of the arsenate groups (counterclockwise at $z = 0$, clockwise at $z = \frac{1}{2}$) which are oriented at 14.0° with respect to the crystal axes in DUAs, whereas the phosphate groups in HUP are at 11.8° . The U—O(3)—As and U—O(3)—P bond angles are $136.0(1)$ and 139.7° respectively. These changes presumably allow better coordination of the U atom by the O atoms of the larger arsenate group.

Very large temperature factors are seen on H(1), H(3) and O(4) in DUAs, and also on O(4) in HUP. Recently it has been suggested that this may be evidence for a conductivity mechanism involving the motion of H_3O^+ ions as a proton carrier (Kreuer, Rabenau & Weppner, 1982). The large temperature factors, however, may also be explained as resulting from the dynamic interchange between H_3O_2^+ and H_4O_2 units by proton hops between the partially filled H(1) sites, as discussed previously (Bernard, Fitch, Howe, Wright & Fender, 1981). The large anisotropy of H(1) along the hydrogen-bond direction suggests that the H atom lies in a broad shallow potential well with considerable interaction with both water oxygens. We do not think, however, that this is closely associated with the conduction pathway because a similar marked anisotropy in H(1) occurs for both $\text{LiUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ (Fitch, Fender & Wright, 1982) and $\text{ND}_4\text{UO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$ (Fitch & Fender, 1983) which both show much lower conductivities (Johnson, Shilton & Howe, 1981).

Further support for the presence of H_3O_2^+ and H_4O_2 units comes from the recent structural determination of DUAs at low temperature (Fitch, Wright & Fender, 1982), where ordering of these species occurs. Moreover, the average O(4)—O(4) linking distance at room temperature, 2.565 (5) Å, is very close to the average O(4) separation of 2.55 (2) Å for these units at 4 K. We have made attempts to refine the separate identities of the H_3O_2^+ and H_4O_2 species at room temperature, in some cases using strict constraints to keep the O(4)—O(4) separation close to those values found at

low temperature, but none were successful. Although slight improvements in the R factor could be achieved, the extra atomic parameters required were only very poorly defined with large e.s.d.'s and high correlation between the various water positional and temperature parameters. The powder diffraction data thus appear to be limited to describing the average oxygen and hydrogen positions.

We thank Dr M. G. Shilton for provision of the $\text{DUO}_2\text{AsO}_4 \cdot 4\text{D}_2\text{O}$ sample.

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The Structure of Deuterated Ammonium Uranyl Phosphate Trihydrate, $\text{ND}_4\text{UO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$ by Powder Neutron Diffraction

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Abstract. $M_r = 447.2$, space group $P4/ncc$, $a = 7.0221(1)$, $c = 18.0912(3)$ Å, $Z = 4$. The structure was determined from a powder neutron diffraction study at room temperature. The profile arising from 257