

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

overlapping reflections was refined to an R_{wp} of 6.9%. The structure is closely related to that of $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$, but there is no clear evidence for discrete NH_4^+ ions. The connection between the structure and the reduction in proton conductivity is discussed in terms of possible mechanisms.

Introduction. The isostructural compounds $\text{HUO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$ (HUAs) and $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ (HUP) have attracted interest due to their high proton conductivity at room temperature (Shilton & Howe, 1977; Howe & Shilton, 1980). From single-crystal X-ray diffraction data, Morosin (1978) determined the structure of HUP [space group $P4/ncc$, $a = 6.995(2)$, $c = 17.491(4) \text{ \AA}$, $Z = 4$] which consists of two-dimensional networks of water molecules, grouped into squares, which alternate with layers of linear UO_2^{2+} and tetrahedral PO_4^{3-} ions (Fig. 1). The U atom of the uranyl group is coordinated equatorially by an O atom from each of four different phosphate ions. The water-molecule networks are located about $z = \frac{1}{4}$ and $z = \frac{3}{4}$ and are connected to each other and to the PO_4^{3-} ions by a network of hydrogen bonds. Each water-molecule O atom participates in four hydrogen bonds, *i.e.* (i) two hydrogen bonds to adjacent water oxygens within a square H(1), (ii) one hydrogen bond to a phosphate oxygen H(2), and (iii) one hydrogen bond to the oxygen of a water molecule in an adjacent square H(3). There are, therefore, 36 H atoms to be distributed over a total of 40 hydrogen bonds per unit cell.

The hydrogen-bond occupancy was obtained from a powder neutron diffraction study on deuterated HUAs by Bernard, Fitch, Howe, Wright & Fender (1981), who showed that all hydrogen bonds are fully occupied except those between water oxygens within a square, H(1), which are on average only $\frac{3}{4}$ occupied. These results also indicated that only one of the two possible positions for the H atom within this latter bond is occupied (Fig. 1) and suggested how the high proton conductivity might be related to the distribution of hydrogen vacancies. The average structure was interpreted in terms of the presence of equal numbers of H_5O_2^+ ions and hydrogen-bonded water dimers ($\text{H}_2\text{O}-\text{H}-\text{OH}$), whose dynamic interconversion provides a simple mechanism for hydrogen mobility.

HUP and HUAs can be cation-exchanged to form a large number of structurally related derivatives (Weigel & Hoffmann, 1976; Fitch, Fender & Wright, 1982), which show generally reduced conductivity (Johnson, Shilton & Howe, 1981). $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, which is the highest hydrate formed when HUP is cation-exchanged with ammonium ion in aqueous solution, shows a 1500-fold decrease in conductivity as compared to HUP.

Single-crystal X-ray diffraction studies on $\text{NH}_4\text{UO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ show the space group to be $P4/ncc$ and it has been postulated that NH_4^+ randomly

substitutes for H_3O^+ in the water squares of HUAs or HUP (Ross & Evans, 1964). Superficially it is easy to see that this could be achieved without large changes in the structure because it is possible to envisage that the four additional H atoms per unit cell simply fill the vacant sites in the HUP structure. The occupancy of the in-square hydrogen bonds would in that case increase from 75% to 100%. However, the presence of a discrete NH_4^+ ion implies there to be four short N—H bonds, which can only be achieved if there is partial ($\frac{1}{4}$) occupancy of the in-square site marked *A* in Fig. 1 with the normal in-square sites in HUP remaining $\frac{3}{4}$ filled.

We report here the results of a powder neutron diffraction study and discuss the consequences for the mechanism of proton conduction in HUP and related compounds.

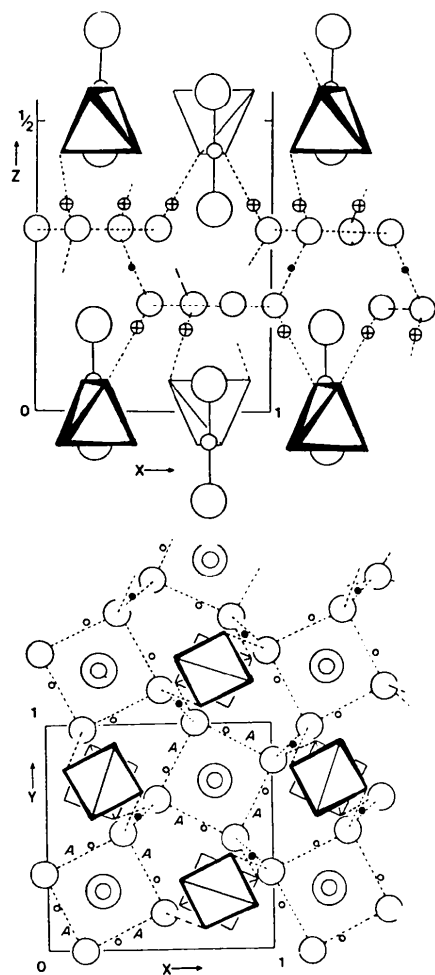


Fig. 1. Projection of the structure of HUAs or HUP along (top) [010], H(1) hydrogens not shown; and (bottom) [001], H(2) hydrogens not shown. Large open circles: uranyl oxygens; medium open circles: water oxygens; tetrahedra: arsenate or phosphate; smaller open circles: uranium; small black circles: H(3) hydrogens; smallest open circles: H(1) hydrogens; crossed circles: H(2) hydrogens. In HUAs the H(1) hydrogen bonds are $\frac{3}{4}$ occupied and there appears to be no occupancy of the alternative hydrogen position (*A*) within the water squares.

Experimental. HUP was precipitated from solution by the published procedure (Childs, Howe & Shilton, 1980). Ammonium ion was substituted for H^+ by stirring with a large excess of 4M ammonium nitrate solution for two days. Deuteration was effected by exchange in 99.85% D_2O . The sample, 11.2 g, was only lightly dried, before being sealed in a standard, 16 mm diameter, thin-walled vanadium sample can. Neutron diffraction studies were performed on the high-resolution powder diffractometer D1A at the high-flux reactor at ILL (Grenoble), at a wavelength of 1.9074 (1) Å as calibrated by a nickel standard. Data were collected in steps of 0.05° over an angular range of $6-156^\circ$ in 2θ at room temperature.

The diffraction pattern was analysed by the method of profile analysis (Rietveld, 1969) as described elsewhere (Fitch, Wright & Fender, 1982).

The scattering lengths used were U 8.50, P 5.1, O 5.80, D 6.67, N 9.40 fm (Bacon, 1975).

The structure was refined in space group $P4/ncc$ using the atomic positions found for deuterated HUAs (Fitch, Bernard, Howe, Wright & Fender, 1983) as starting parameters. All the hydrogen bonds were fully occupied and the nitrogen and water oxygen atom O(4) were refined identically. The refinement proceeded satisfactorily, except for the hydrogen atom H(3) which provides the three-dimensional linking between adjacent water squares and which developed a very large B_{33} temperature parameter. In deuterated HUAs, H(3) was constrained to the special crystallographic position $8(f)$ ($\bar{x}, x, \frac{1}{4}$) midway between the water squares, because here it gave the most satisfactory description of the average scattering density arising from the statistical superposition of the disordered $H_3O_2^+$ ions and water dimers. In $ND_4UO_2PO_4 \cdot 3D_2O$ there is no such disordering scheme and the distance between water oxygens in adjacent squares, 2.738 (7) Å, is much larger than the value of 2.4 Å which is generally considered to be the maximum O—O separation for a

centred and symmetric hydrogen bond (Thomas & Liminga, 1978). H(3) was therefore allowed to refine in the general position 16(g) (x, y, z) which corresponds to half-occupancy of equivalent hydrogen-bond sites on either side of the symmetry axis between the two water squares. Refinement of the occupancy of the water molecules showed no significant deviation from 3, in agreement with Weigel & Hoffmann (1976) and Johnson *et al.* (1981) who have performed TGA measurements. Thus the refinement involved a total of 56 atomic positional and thermal parameters for $ND_4UO_2PO_4 \cdot 3D_2O$, the scale factor, a zero point and two lattice parameters, three half-width parameters, asymmetry and preferred orientation parameters to correct for a small amount of alignment of the plate-like crystallites normal to [001], and finally the scattering length of deuterium. There were 257 reflections. The refinement converged to give $R_f = 5.4$, $R_{wp} = 6.9$, $R_p = 10.2$, $R_E = 6.3\%$, and indicated the degree of deuteration to be 99.5 (1)%. The structural parameters are given in Table 1, the observed and calculated profiles in Fig. 2.* Average bond lengths and angles are given in Table 2. A further refinement involving separate parameters for the nitrogen and water oxygens produced only a minor decrease in R factor, and physically unreal temperature factors for both atoms.

Discussion. The structure closely resembles that of HUP (Morosin, 1978) with linear UO_2^{2+} ions coordinated equatorially by the O(3) atoms of four slightly distorted PO_4^{3-} ions. The bond distances and angles of these groups are very similar in the two compounds. There are modifications, however, to the water squares with a general increase in the lengths of the O—O

* The numerical data corresponding to Fig. 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38163 (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 $ND_4UO_2PO_4 \cdot 3D_2O$ at room temperature in space group $P4/ncc$ (origin at $\bar{1}$) with $a = 7.0221$ (1), $c = 18.0912$ (3) 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 thermal parameters are in Å², and e.s.d.'s are given in parentheses.

	Position	Point symmetry	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	4(c)	4	$\frac{1}{4}$	$\frac{1}{4}$	0.0479 (2)	0.7 (1)	0.7 (1)	2.5 (2)	0	0	0
As	4(b)	$\bar{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0.1 (1)	0.1 (1)	2.8 (3)	0	0	0
O(1)	4(c)	4	$\frac{1}{4}$	$\frac{1}{4}$	0.1470 (3)	1.4 (1)	1.4 (1)	2.5 (2)	0	0	0
O(2)	4(c)	4	$\frac{1}{4}$	$\frac{1}{4}$	-0.0512 (3)	2.3 (2)	2.3 (2)	1.4 (2)	0	0	0
O(3)	16(g)	1	0.5771 (3)	0.2257 (3)	0.0500 (2)	0.7 (1)	1.7 (1)	2.4 (2)	-0.3 (1)	-0.1 (1)	0.2 (1)
N/O(4)	16(g)	1	0.1611 (5)	0.9809 (5)	0.3149 (3)	4.1 (2)	3.5 (2)	1.9 (2)	-0.7 (1)	-0.0 (2)	0.6 (2)
H(1)	16(g)	1	0.3212 (10)	0.0403 (6)	0.3191 (3)	14.0 (4)	6.5 (2)	4.1 (2)	6.0 (2)	0.2 (2)	-0.6 (2)
H(2)	16(g)	1	0.5947 (5)	0.1394 (4)	0.3592 (3)	3.6 (2)	3.8 (2)	3.5 (2)	-0.2 (1)	-0.9 (2)	0.2 (1)
H(3)	16(g)*	1	0.3794 (11)	0.5890 (11)	0.2697 (4)	5.1 (5)	3.1 (3)	0.8 (8)	-0.1 (3)	0.8 (4)	2.2 (4)

* $\frac{1}{2}$ occupied.

Table 2. Bond distances (Å) and angles (°) for $\text{ND}_4\text{UO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$ at room temperature

E.s.d.'s are given in parentheses.

(1) Uranyl ion		(3) Water/ammonium	
U—O(1)	1.793 (6)	O(4)—H(1)	1.201 (8)
U—O(2)	1.792 (6)	O(4)—H(2)	0.974 (6)
U—O(3)	2.303 (2)	O(4)—H(3)	0.995 (9)
O(1)—U—O(2)	180	O(4)—O(4) ^(c)	2.814 (5)
O(1)—U—O(3)	89.0 (1)	O(4)—O(4) ^(d)	2.738 (7)
		H(1)—O(4)	1.630 (7)
(2) Phosphate ion		H(2)—O(3)	1.932 (5)
P—O(3)	1.524 (2)	H(3)—O(4)	1.762 (9)
O(3)—P—O(3) ^(a)	107.1 (1)	O(4)—O(3)	2.903 (5)
O(3)—P—O(3) ^(b)	110.6 (1)	H(1)—O(4)—H(2)	106.5 (5)
U—O(3)—P	140.9 (2)	H(1)—O(4)—H(3)	119.4 (6)
		H(2)—O(4)—H(3)	111.3 (6)
		O(4)—H(1)—O(4)	167.2 (5)
		O(3)—H(2)—O(4)	174.2 (4)
		O(4)—H(3)—O(4)	166.0 (8)

Notes: (a) Both O(3) have same *z* values. (b) O(3) have opposite *z* values. (c) Side-of-square distance. (d) Inter-square linking distance.

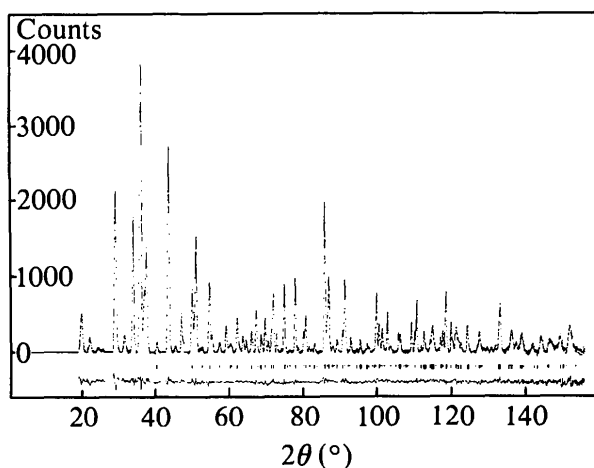


Fig. 2. Observed (points), calculated (full curve) and difference profiles for $\text{ND}_4\text{UO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$ at 1.9074 Å on D1A at room temperature.

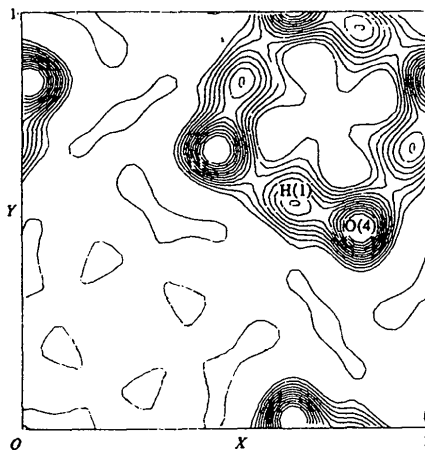


Fig. 3. Fourier section based on observed intensities and calculated phases for $\text{ND}_4\text{UO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$ at $z = 0.19$.

hydrogen-bonded distances. This presumably results from the general decrease in average electronegativity of the water squares by the disordered substitution of a quarter of the oxygens by nitrogen. For the hydrogen bond between water molecules within a square, these effects are largely compensated for by the increase in fractional occupancy of this site to 1 from $\frac{3}{4}$. Hence, in HUP the lengths of the H(1), H(2) and H(3) hydrogen bonds are 2.81 (2), 2.83 (1) and 2.56 (2) Å respectively (Morosin, 1978), whereas for $\text{ND}_4\text{UO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$ they are 2.814 (5), 2.903 (5) and 2.738 (7) Å. The difference in lattice parameters between the two compounds is therefore most marked in the *c* direction.

The parameters given in Table 1 represent a structural model similar to that of HUAs (Fitch, Bernard, Howe, Wright & Fender, 1983) or $\text{LiUO}_2\text{-AsO}_4 \cdot 4\text{H}_2\text{O}$ (LiUAs) (Fitch, Fender & Wright, 1982) in which the H atoms within a square occupy only one of the two possible positions between the water oxygens (Fig. 1). The observed Fourier section, Fig. 3, which shows a very close resemblance to that found for HUAs (Bernard, Fitch, Howe, Wright & Fender, 1981) or LiUAs, indicates that this is a reasonable assumption. In all three compounds there is a large anisotropy of H(1) along the direction of the hydrogen bond, suggesting that the potential well between the water oxygens is broad and shallow. A refinement which allows partial occupation of the alternative hydrogen position (site *A* in Fig. 1) leads, in all three cases, to some occupancy of that site, a considerable reduction in the H(1) temperature factor, yet no significant decrease in *R* factor. We are not convinced that the occupancy of the site is real, and suspect that it may be merely an artifact arising from a genuinely large thermal anisotropy of H(1). We base this observation not only on the fact that there is no decrease in R_{wp} but also on the appearance of the Fourier sections themselves. If, on the other hand, site *A* is unoccupied in $\text{ND}_4\text{UO}_2\text{PO}_4 \cdot 3\text{D}_2\text{O}$, it implies that there are no discrete NH_4^+ ions in the compound and the predominant species would have to be H_3O^+ and NH_3 . Although crystal-field effects may disturb the normal proton affinities of NH_3 and H_2O , this is such a surprising result that it would be worthwhile making a separate study at 4 K; the reduction in the H(1) temperature factor would allow a closer examination of the scattering density near site *A*.

Conductivity

Recently it has been suggested that the high conductivity observed in HUP or HUAs may be explained not in terms of a basic Grotthuss-type mechanism involving proton hops and water-molecule reorientations (Bernard, Fitch, Howe, Wright & Fender, 1981; Bernard, Fitch, Wright, Fender & Howe, 1981) but by a 'vehicle mechanism'. The proton is envisaged to migrate bonded to a charged group such

as H_3O^+ (or NH_4^+) rather than as a single H^+ (Kreuer, Rabenau & Weppner, 1982). It is, however, not easy to envisage by this mechanism why such a marked reduction in conductivity should occur for the ammonium-substituted compound. The number of potential hydrogen carriers (whether H_3O^+ or NH_4^+) is the same in both systems. On the other hand, the number of hydrogen vacancies in $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$ is drastically reduced by the filling of the in-square hydrogen bonds, suggesting that a mechanism involving proton jumps between filled and unfilled sites is dominant.

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A Glaserite-Type Structure: Calcium Tripotassium Hydrogenbis(phosphate), $\text{CaK}_3\text{H}(\text{PO}_4)_2$

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Abstract. $M_r = 348.34$, monoclinic, space group $C2/m$, $a = 9.878$ (1), $b = 5.735$ (1), $c = 7.436$ (1) Å, $\beta = 94.28$ (1)°, $V = 420.08$ Å³, $Z = 2$, $D_m = 2.77$, $D_x = 2.754$ Mg m⁻³ at 298 K, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 2.65$ mm⁻¹. Final $R = 0.017$ for 512 observed reflections. The structure consists of columns of cations, Ca and K(1), and columns of cations and anions, K(2) and PO_4 . The arrangement of these columns in a pseudo-hexagonal form is similar to that of glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$, e.g. $\alpha\text{-Ca}_3(\text{PO}_4)_2$ (Mathew, Schroeder, in a symmetric hydrogen bond across a crystallographic center of inversion to form a dimeric $[\text{H}(\text{PO}_4)_2]$ unit.

Introduction. A number of calcium phosphates are known to have structures related to glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$, e.g. $\alpha\text{-Ca}_3(\text{PO}_4)_2$ (Mathew, Schroeder, Dickens & Brown, 1977), $\text{Ca}_5(\text{SiO}_4)(\text{PO}_4)_2$ (Dickens & Brown, 1971*a*), and $\text{Ca}_7\text{Mg}_9(\text{Ca},\text{Mg})_2(\text{PO}_4)_{12}$ (Dickens & Brown, 1971*b*). However, none of these compounds contains HPO_4 groups. $\text{CaK}_3\text{H}(\text{PO}_4)_2$, which contains

an acidic PO_4 group, has been proposed to be related to glaserite (Brown & Fowler, 1967; Grenier, Durif & Martin, 1969; Dickens & Brown, 1972). A structural study was therefore undertaken to elucidate any relationship with other glaserite-type compounds.

Experimental. Crystals were prepared by the method used by Frazier, Smith, Lehr & Brown (1962). The X-ray powder pattern, refractive indices, cell parameters and space group obtained for this study agreed with the reported values (Frazier *et al.*, 1962). Precession photographs showed monoclinic symmetry $2/m$, although they showed marked pseudotrigonal symmetry. Systematic absences of hkl for $h+k = 2n+1$ indicated the possible space groups Cm , $C2$ and $C2/m$. The centrosymmetric space group $C2/m$, initially chosen, was confirmed by the structure analysis and refinements.

Thin platy crystal $0.02 \times 0.14 \times 0.18$ mm used for measurement of precise cell constants and three-dimensional intensity data, automatic four-circle dif-