# The Structure of Anhydrous Uranyl Chloride by Powder Neutron Diffraction

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Other workers have previously studied the structure of anhydrous $UO_2Cl_2$ by X-ray powder diffraction methods. In this earlier work, the oxygen atom locations could not be determined because of the heavy scattering by the uranium atom, and these were deduced from geometrical considerations. The present neutron powder diffraction analysis, with the profile fitting technique, has revealed errors of 0·56 and 0·17 Å in the earlier proposed oxygen positions, and 0·16 Å in the chlorine location. The interatomic distances and angles from the neutron diffraction analysis are normal.

## Introduction

The crystal structure of $UO_2Cl_2$ has been the subject of controversy for many years. Early reports (Baenziger & Rundle, 1944; Dunn, 1956; Johnson, Butler, Powell & Nottorf, 1944) differ in the data recorded from the X-ray powder diffraction pattern of $UO_2Cl_2$, and in the interpretation of the data. Also the X-ray powder diffraction pattern of sublimed $UO_2Cl_2$ is reported to differ from that of unsublimed $UO_2Cl_2$ powder (Johnson *et al.*, 1944). The system has been investigated more recently by Debets (1968), who determined the uranium and chlorine locations from Patterson syntheses of the X-ray powder data. The oxygen locations, unobservable because of the heavy X-ray scattering by uranium, were deduced from geometrical considerations.

In view of the differing results reported above, and since the oxygen atom positions had never been observed directly, it was decided that a neutron diffraction study of the system would be worth while. The favourable neutron scattering factors permit observation of all atomic positions in the unit cell.

## Experimental

Since a sufficiently pure form of $UO_2Cl_2$ is not available commercially, a sample was prepared in the laboratory. The starting product for the preparation was a particularly reactive form of $UO_3$ that had been prepared by thermal decomposition of $UO_4(H_2O)_2$. This was reduced to $UO_2$ using $H_2$ (Katz & Rabinowitch, 1951). The $UO_2$ so produced was very reactive and burned readily in air. This $UO_2$ was then converted to $UCl_4$ by vapour phase chlorination using $CCl_4$ (Carter, 1954). Finally, the $UCl_4$ was converted to $UO_2Cl_2$ by oxidation using elemental oxygen (Johnson, 1944). A feature of the preparative method used was that all the reactions listed above were carried out sequentially in the one reactor. This avoided contamination of the reactive intermediates by unnecessary handling. When the $UO_2Cl_2$ was finally prepared it was sealed into a glass ampoule that was attached directly to the preparative reactor, and stored in this ampoule until required. This avoided hydrolysis of the sample. All subsequent handling of the sample was carried out in a dry box. Uranyl chloride is thermally unstable (John-
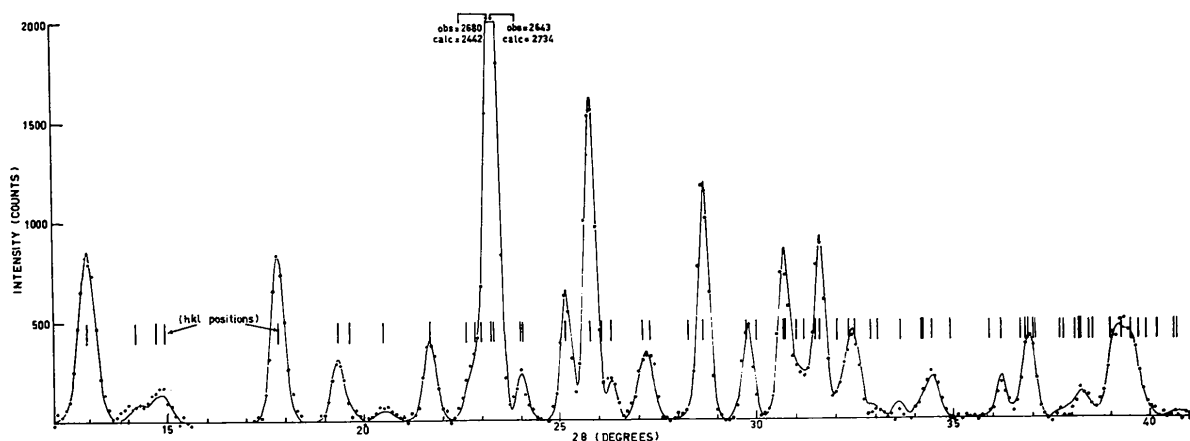


Fig. 1. Observed and calculated neutron diffraction pattern profile for anhydrous $UO_2Cl_2$.

son *et al.*, 1944), and so a single crystal sufficiently large for structural analysis could not be prepared by sublimation or sintering. Consequently, structural information must be obtained from studies of the powder.

To collect the neutron diffraction pattern the sample was placed in a polytrifluorochloroethylene tube. The pattern was obtained on HIFAR, the AAEC research reactor, using the double-crystal technique (Caglioti, 1970). The range of the pattern was $12° < 2\theta < 42°$ with $\lambda = 1.077$ Å.

### Results and discussion

The crystal data reported by Debets (1968) are given in Table 1. The neutron diffraction pattern, which is shown in in Fig. 1, was in agreement with the unit cell of Debets, and consistent with the space groups *Pnma* or *Pn2a*. With these neutron data, a satisfactory refinement of the structure proposed by Debets in the higher symmetry space group *Pnma* was obtained. The

refinement was carried out using the profile analysis technique of Rietveld (1967), which is considered to be the best available method. The unit-cell dimensions of Debets were used. The computer program used was a modified version (J. C. Taylor & G. W. Cox, unpublished work) of the Busing–Levy least-squares program (Busing, Martin & Levy, 1962) and the peaks making up the diffraction pattern were assumed to be of Gaussian profile. The neutron scattering lengths used (Neutron Diffraction Commission, 1969) were $b_U = 0.84$, $b_{Cl} = 0.96$ and $b_O = 0.577$ in units of $10^{-12}$ cm. An overall isotropic Debye–Waller factor $B$ was used. After several cycles, the agreement between the observed and calculated neutron pattern profiles (Fig. 1) was excellent, indicating that (*a*) the data were good and preferred orientation effects were negligible and (*b*) that the peaks were Gaussian. The criterion of fit, $\chi = [\sum w(I_o - I_c)^2/(NO - NV)]^{1/2}$, which should be unity for perfect agreement between experiment and theory, was 1.029. As a satisfactory structure was found by this method in the higher symmetry space
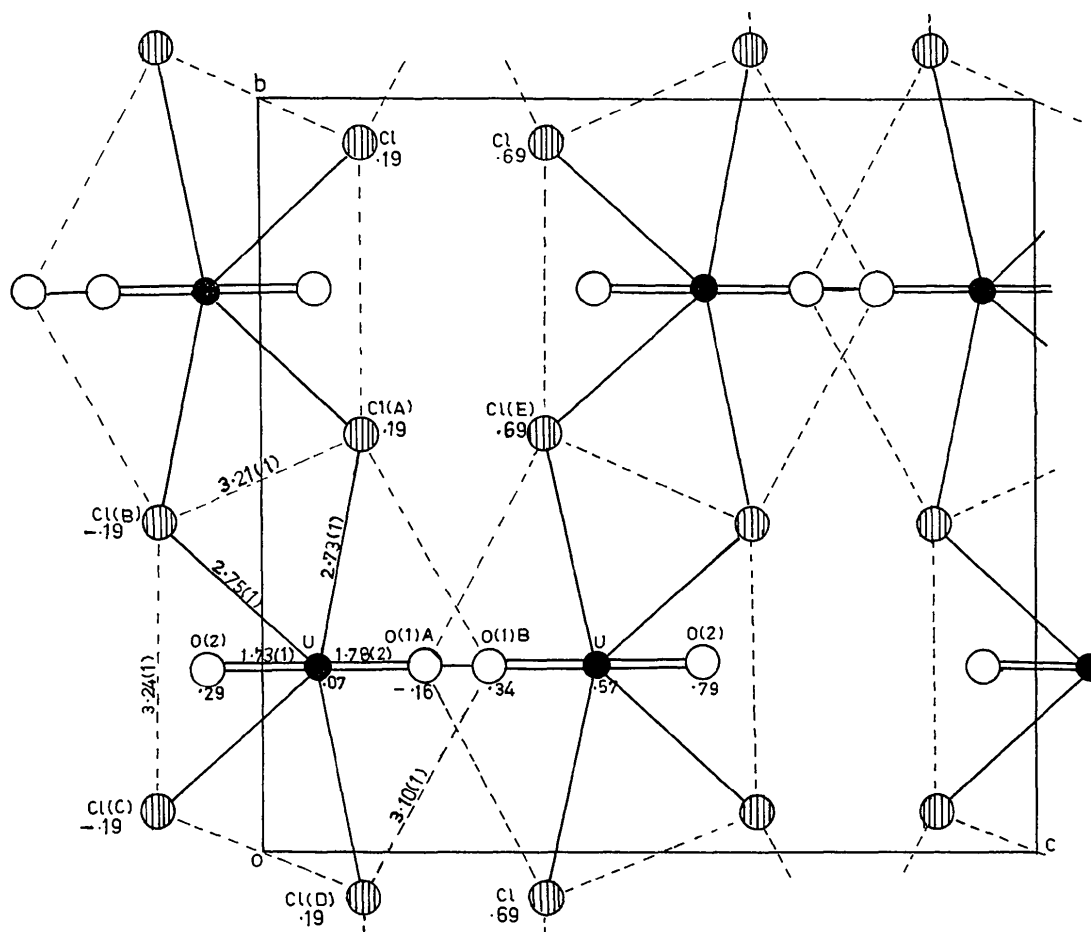


Fig. 2. The crystal structure of anhydrous $UO_2Cl_2$. The U atoms are shown as solid circles, Cl atoms as shaded circles, and O atoms as open circles. The $x$ coordinates of some of the atoms are shown.

group, the alternative low symmetry space group $Pn2a$ was not considered further.

## Table 1. Crystal data for anhydrous $UO_2Cl_2$

Orthorhombic, space group $Pnma$ ($D_{2h}^{16}$) or $Pn2a$ ($C_{2v}^{9}$);
    $a = 5.725$ (1), $b = 8.409$ (2), $c = 8.720$ (2) Å.
M.W. 340·93, $U = 419.79$ Å$^3$, $D_m = 5.28$ g cm$^{-3}$ at 25 °C,
    $D_x = 5.394$ g cm$^{-3}$, m.p. 578 °C.

The neutron parameters are compared with the X-ray parameters in Table 2. The neutron parameters are more reliable because of the more advantageous neutron scattering factors. The X-ray position of the O(2) atom was found to be in error by 0·56 Å, by comparison with the neutron coordinates. The X-ray and neutron uranium locations were in good agreement, as expected, but the chlorine locations differed by 0·16 Å. The chlorine atom is a relatively heavy neutron scatterer; thus the neutron chlorine location was more reliable than the X-ray location.

## Table 2. Neutron (ND) and X-ray (XR) diffraction parameters in anhydrous $UO_2Cl_2$ and the differences $\Delta$ between the neutron and X-ray locations

|      | Method | $x(\times 10^3)$ | $y(\times 10^3)$ | $z(\times 10^3)$ | $\Delta$ (Å) |
|------|--------|--------|--------|--------|--------|
| U    | ND     | 68 (2) | $\frac{1}{4}$ | 66 (1)  | 0·02 |
|      | XR     | 67 (2) | $\frac{1}{4}$ | 64 (1)  |      |
| O(1) | ND     | −160 (2) | $\frac{1}{4}$ | 206 (2) | 0·17 |
|      | XR     | −130 (22) | $\frac{1}{4}$ | 208 (11) |     |
| O(2) | ND     | 294 (2) | $\frac{1}{4}$ | −66 (2) | 0·56 |
|      | XR     | 279 (19) | $\frac{1}{4}$ | −3 (10) |      |
| Cl   | ND     | 192 (1) | 557 (1) | 123 (1) | 0·16 |
|      | XR     | 170 (5) | 545 (3) | 124 (3) |      |

Debye–Waller factor $= 0.8$ (3) Å$^2$ (XR) and 1·4 (2) Å$^2$ (ND).

The crystal structure of $UO_2Cl_2$ (anhydrous) is illustrated in Fig. 2. The $U^{VI}$ coordination polyhedron is a pentagonal bipyramid, with uranyl oxygen atoms O(1)$A$ and O(2)$A$ at the apices. The atoms Cl($A$), Cl($B$), Cl($C$), Cl($D$) and O(1)($B$) form the equatorial pentagon. The pentagons, by sharing Cl–Cl edges, form chains parallel to **b**. Bonding in the **a** and **c** directions is achieved by the sharing of O(1) atoms between neighbouring polyhedra, the O(1) atom having a dual role as the apical uranyl oxygen in one bipyramid and the equatorial oxygen atom of a neighbouring bipyramid.

The neutron bond lengths and angles, shown in Table 3, are normal. The uranyl distances are U–O(1)($A$) = 1·78 (2) and U–O(2)($A$) = 1·73 (1) Å. The longer uranyl distance for O(1) is probable in view of the O(1) dual bonding role mentioned above. O(1) is also bonded to another uranium atom in an equatorial bond of length 2·52 (2) Å, whereas O(2) is bonded to one uranium atom only.

The U–Cl distances are 2·73 (1) and 2·75 (1) Å in the equatorial plane. These U–Cl distances may be compared with the U–Cl distances of 2·62 Å in $Cs_2UO_2Cl_4$ (Hall, Rae & Waters, 1966) and 2·42 Å in $UCl_6$

## Table 3. Bond lengths and angles in anhydrous $UO_2Cl_2$

Bonds to uranium

| | |
|---|---|
| U–Cl ($A$) | 2·73 (1) Å |
| U–Cl ($B$) | 2·75 (1) |
| U–O(1) ($A$) | 1·78 (2) (uranyl) |
| U–O(1) ($B$) | 2·52 (2) (pentagon) |
| U–O(2) ($A$) | 1·73 (1) (uranyl) |

Contacts around pentagon

| | |
|---|---|
| Cl ($A$)–Cl ($B$) | 3·21 (1) Å |
| Cl ($B$)–Cl ($C$) | 3·24 (1) |
| Cl ($A$)–O(1) | 3·10 (1) |

Other distances

| | |
|---|---|
| O(1) ($A$)–O(1) ($B$) | 2·96 (1) Å |
| Cl ($A$)—Cl ($E$) | 3·62 (1) |
| O(1) ($B$)–Cl ($E$) | 3·36 (1) |

Pentagonal angles in ring ($\sim 72°$)

| | |
|---|---|
| Cl ($A$)–U–Cl ($B$) | 71·9 (2)° |
| Cl ($B$)–U–Cl ($C$) | 72·2 (3) |
| Cl ($D$)–U–O(1) ($B$) | 72·4 (2) |

Uranyl angle

| | |
|---|---|
| O(2) ($A$)–U–O(1) ($A$) | 178·8 (8) |

Angles in bipyramid ($\sim 90°$)

| | |
|---|---|
| O(1) ($A$)–U–Cl ($A$) | 93·8 (3)° |
| O(1) ($A$)–U–Cl ($B$) | 90·8 (5) |
| O(1) ($A$)–U–O(1) ($B$) | 85·1 (4) |
| O(2) ($A$)–U–Cl ($A$) | 85·8 (3) |
| O(2) ($A$)–U–Cl ($B$) | 90·2 (5) |
| O(2) ($A$)–U–O(1) ($B$) | 93·7 (7) |

See Fig. 2 for nomenclature.

(Zachariasen, 1948). The other contact distances in the structure are 2·96 Å or greater. It is interesting to note that $UO_2Cl_2$ adopts a completely different structure from that of $UO_2F_2$ (Atoji & McDermott, 1970), because of the differing size of the chlorine and fluorine atoms. Six chlorine atoms cannot fit around the equator of the uranyl group, whereas six fluorine atoms can be arranged in the uranyl equatorial plane.

The pentagonal angles are close to the 72° angle for a regular pentagon, and the O–U–Cl bonds and O (uranyl)–U–O(pentagonal) bonds are close to 90°. As expected, the uranyl angle is not significantly different from 180°.

If the polyhedra were isolated, the uranium atom and the five pentagonal atoms in a polyhedron should be coplanar. However, as described above, chlorine and O(1) atoms are shared between adjacent polyhedra. A least-squares plane was calculated through the atoms U, Cl($A$), Cl($B$), Cl($C$), Cl($D$) and O(1)($B$) using the method of Schomaker, Waser, Marsh & Bergman (1959) and a computer program written at this Establishment (B. M. Craven and M. M. Elcombe, unpublished work). The equation of the plane, in perpendicular form, with absolute coordinates, was found to be:

$$0.7465X - 0.6654Z = -0.0578.$$

The distances of the six atoms from their least-squares plane are given in Table 4, and it is seen that the uranium and pentagon atoms are not coplanar.

Table 4. *Distances of uranium and pentagon atoms from their least-squares plane*

| | Distance ($\text{Å} \times 10^3$) | Error ($\text{Å} \times 10^3$) |
|---|---|---|
| U | $-36$ | 14 |
| Cl ($A$), Cl ($D$) | 164 | 10 |
| Cl ($B$), Cl ($C$) | $-49$ | 10 |
| O(1) ($B$) | $-195$ | 21 |

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# Alkali Metal Ordering and Hydrogen Bonding in the System KHSO₄–RbHSO₄: the Crystal Structures of KₓRb₁₋ₓHSO₄ (0·3 < x < 0·55) and RbHSO₄

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The crystal structures of $K_xRb_{1-x}HSO_4$, $x=0.55$, and of $RbHSO_4$ have been determined by X-ray single-crystal analysis. $K_xRb_{1-x}HSO_4$, $x=0.55$, is monoclinic with space group $P2_1/c$ and has the unit-cell dimensions $a=7.07$, $b=14.10$, $c=8.17$ Å, $\beta=103.9$. As a structure type, $K_xRb_{1-x}HSO_4$ exists for the range $0.30 < x < 0.55$. For $x=0.55$ all of the $Rb^+$ present is ordered into one of the two sites available to the alkali metals. $RbHSO_4$ is also monoclinic, space group $P2_1/c$, and has unit-cell dimensions $a=14.29$, $b=4.61$, $c=14.76$ Å, $\beta=120.4°$. The $K_xRb_{1-x}HSO_4$ structure type has a layer structure, and exhibits the same overall arrangement of alkali metals and sulphate groups within each layer as does $RbHSO_4$ in (010) projection. These layers build into a three-dimensional structure intermediate between that of $KHSO_4$ and $RbHSO_4$.

## Introduction

The sulphates of potassium, rubidium and caesium all have the orthorhombic $K_2SO_4$ structure (Wyckoff, 1965). Lithium sulphate (Albright, 1932) has a monoclinic tetramolecular structure (Li is a much smaller ion than K, Rb or Cs), while sodium sulphate is pleomorphic with five different modifications, one of which, $Na_2SO_4(III)$ (Fischmeister, 1954), resembles $K_2SO_4$. It is noteworthy that many mixed alkali metal–alkaline earth compounds of the stoichiometry $ABMO_4$, including phosphates, arsenates and vanadates, also have the $K_2SO_4$ structural arrangement, thus demonstrating an analogy between normal phosphate and sulphate groups.

Except for $KHSO_4$ (Loopstra & MacGillavry, 1958) the structures of the alkali metal acid sulphates are not

known in any detail. The present paper discusses the structures of two compounds found in the $KHSO_4$–$RbHSO_4$ system, $K_{0.55}Rb_{0.45}HSO_4$ and $RbHSO_4$.

## Experimental

Crystals of the acid sulphates were prepared by dissolving $Rb_2SO_4$ alone, or by mixing in an appropriate molar ratio with $K_2SO_4$ in sulphuric acid and adding a little water. On cooling to room temperature, well-shaped crystals were formed, most of which were rhombic plates of varying thickness although in the case of $RbHSO_4$ a few were needle shaped. Rubidium to potassium metal ratios for the single phases crystallized from these solutions were obtained from molecular weights determined by simple acid-base titrations on crystals which had been well washed