X-Ray Investigations on Uranyl Hydroxides

I. The Crystal Structure of $\beta$-UO$_2$(OH)$_2$

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$\beta$-UO$_2$(OH)$_2$ has a face-centered orthorhombic cell with the dimensions $a = 6.295 \pm 0.005$ Å, $b = 5.636 \pm 0.005$ Å, and $c = 9.32_{+}^{+} \pm 0.01$ Å. The unit cell contains four formula units. The atomic positions can be described by the space group No. 69 Fmmm as given on p. 678. The structure is built up of pseudotetragonal layers connected by van der Waals contact between the UO$_4^{2+}$ groups. Every uranium atom is joined through four atoms to its neighbouring U atoms. The positions of the oxygen atoms were inferred from geometrical arguments and considerations of the strength of the U–O bonds.

In connection with an X-ray investigation of "uranates" undertaken at these institutes by Bergström and Sillén$^1$, it was of interest to know the crystal structure of a pure uranyl hydroxide. However, in the literature only a preliminary structure determination of a uranyl hydroxide, viz. $\alpha$-UO$_2$(OH)$_2$, has been published (Zachariasen)$^2$. The positions of the uranium atoms in the unit cell are given, but the parameters of the oxygen atoms are not discussed. Other investigations$^5$ are mainly concerned with the identification of different phases of UO$_2$(OH)$_2$(H$_2$O)$_2$. Thus, since no complete structure determination seems to have been published, we thought that an investigation of such a structure would be worth while.

In Gmelin’s Handbuch some papers on the preparation of crystalline uranyl hydroxides are cited. The best of the methods described seemed to be thermal hydrolysis of uranyl acetate solutions$^3,4$. In this way we were able to prepare some different uranyl hydroxides in a crystalline form suitable for single crystal X-ray work. The structure determination of one of them is dealt with here. It has been called $\beta$-UO$_2$(OH)$_2$ for reasons to be given at the end of this paper. Structure studies on some of the other phases will be published in subsequent papers.
PREPARATION OF THE CRYSTALS

A solution of uranyl acetate containing 1 g UO₂(CH₃COO)₂ in 100 ml water was heated in a sealed glass tube at 105—110°C for about 120 hours, after which a yellow, crystalline precipitate had formed. The crystals were filtered off and dried in air. Under the microscope they proved to be either yellow, transparent, six-sided plates or yellow needles about 0.1—0.2 mm in length. They often grew together in clusters.

X-ray powder photographs were taken with focusing cameras of the Phragmén type, first of the original mixture of plates and needles, and then only of picked-out plates. The same patterns were obtained. However, on comparing the observed values of sinθ with those calculated from the cell dimensions obtained from single crystal photographs, we found that some of the weaker lines of the powder photograph did not fit in. As no indication of a superstructure was found in the single crystal photographs, we concluded that the preparation contained one or more phases as impurities. We also tried to index the extra lines assuming the impurity to be α-UO₂(OH)₄, but the attempt was not successful.

Analysis. Since the crystals were prepared from a solution of uranyl acetate we tested them for acetate ions with lanthanum nitrate and iodine before they were analysed quantitatively. The result was negative and we concluded that the compound contained only uranium, oxygen, and hydrogen. The uranium content was determined by igniting the sample at 750°C and weighing the residue as U₃O₈. The water was determined by Brush* and Penfield's† method, described by Kolthoff and Sandell‡.

<table>
<thead>
<tr>
<th>Found</th>
<th>Calculated for UO₂(OH)₄</th>
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<tr>
<td>% UO₂</td>
<td>93.0</td>
</tr>
<tr>
<td>% H₂O</td>
<td>5.9</td>
</tr>
<tr>
<td>Density</td>
<td>5.72</td>
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The analyses indicate the formula UO₂(OH)₄. Since, however, the powder photographs show that the preparation contains more than one phase the analytical data alone do not allow a definite conclusion. As will be shown below, the geometrical arguments for the positions of the oxygen atoms also support the formula UO₂(OH)₄.

UNIT CELL AND SPACE GROUPS

A crystal was set with the longest diagonal of the plate as rotational axis; it was called the a axis. Using CuK radiation, rotation and the following Weissenberg photographs were taken: 0kl (with 4 × 23 reflections registered), 1kl (with 4 × 16 reflections registered) and 2kl (with 4 × 19 reflections registered). From these photographs the following approximate cell dimensions of the orthorhombic unit cell were found: \( a = 6.2 \pm \AA \), \( b = 5.6 \pm \AA \), and \( c = 9.9 \pm \AA \). The c axis is perpendicular to the plate. Rotation and Weissenberg photographs were also taken of the needles, which proved to have the same cell dimensions and symmetry as the plates. The axis of the needles was [110].

From the powder photographs (cf. Table 1) more accurate cell dimensions were calculated:

\[
\begin{align*}
\alpha &= 6.295 \pm 0.005 \, \text{Å} \\
\beta &= 5.638 \pm 0.005 \, \text{Å} \\
\gamma &= 9.922 \pm 0.01 \, \text{Å} \\
V &= 352.4 \, \text{Å}^3
\end{align*}
\]

All reflections hkℓ with \( h + k = \text{odd} \) or \( k + l = \text{odd} \) are systematically absent. This is characteristic of the space groups No. 69 Fmmm, No. 42

* Acta Chem. Scand. 10 (1956) No. 4
Table 1. Powder photographs of $\beta$-UO$_3$(OH)$_n$. CrK radiation $\lambda_{CrK\alpha} = 2.2999$ Å.

<table>
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<tr>
<th>h k l</th>
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<th>10$\sin^2$$\Theta$</th>
<th>I</th>
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The horizontal lines mark the boundaries between the angular ranges of the three different focussing cameras used. Reflections systematically absent in the space group $Fmm2$ have been omitted. Reflections coinciding with $\beta$ reflections are given in brackets. Reflections having no corresponding $10\sin^2\Theta$ are assumed to belong to the phase not investigated. In the powder photographs there is an absorption and orientation effect favouring reflections with high $l$ indices.

$Fmm2$, and No. 22 $F222$. The reflections recorded in the Weissenberg photographs were all strong and of much the same intensity, apart from the general decrease in intensity always found with increasing $\Theta$.

**Positions of the uranium atoms**

The plausible space groups demand that there should be $4n$ uranium atoms in the unit cell (where $n$ is an integer). From the volume of the cell we can calculate that, for $n = 1$, $d_{calc} = 5.73$ (assuming the formula as UO$_3$(OH)$_3$). As the observed density is 5.72 and as the major part of the preparation seems to consist of the phase investigated, we could then safely say that there are

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4 U atoms per unit cell. We may arbitrarily choose their positions as 4(a) in Fmmm, 4(a) in F222 or 4(a) with z = 0 in Fmm2. All these positions have the coordinates 000; \( \frac{1}{4} \frac{1}{4} 0 \); \( 0 \frac{1}{4} \frac{1}{4} \), corresponding to a face-centered uranium lattice.

Previous data on uranium-oxygen coordination

In addition to the uranium atoms there are oxygen and hydrogen atoms in the unit cell. The positions of these light atoms could not be determined from the intensities of the reflections, and thus they had to be inferred from considerations of the interatomic distances and the bond strength of the U—O bond.

All oxygen compounds of U(VI) hitherto studied by X-ray methods, except a-UO₂, seem to contain uranyl ions UO₂⁺. In the "uranates" investigated (CaUO₄, SrUO₄, BaUO₄, Li₂UO₄, Na₂UO₄, K₂UO₄, MgUO₄), each uranium atom is connected by oxygen bridges forming \((\text{UO}_2\text{O}_4)^{2-}\)-layers or chains perpendicular, or almost perpendicular, to the uranyl groups.

In BaUO₄ and MgUO₄ each oxygen bridge connects two neighbouring uranyl groups, resulting in pseudo-tetragonal \((\text{UO}_2\text{O}_4)^{2-}\)-layers with single oxygen bridges for BaUO₄ and \((\text{UO}_2\text{O}_4)^{2-}\)-chains with double oxygen bridges for MgUO₄. The distances U—Obridge are 2.12—2.22 Å.

In the other "uranates" mentioned each UO₂⁺ group is connected with its next six UO₂⁺ neighbours by oxygen atoms, each of which is shared between three uranyl groups, and thus a pseudo-hexagonal lattice is formed. In these compounds the distances U—Obridge are 2.3 Å.

In a-UO₂ the coordination uranium-oxygen is the same as in the pseudo-hexagonal "uranates". However, the "uranyl" oxygen atoms are shared between two uranium atoms forming chains of U—O—U—... instead of discrete UO₂⁺ groups.

A compilation of all observed U—O distances has been given by Zachariassen. He found that they all lay on a smooth curve when they were plotted as a function of the bond strength s of the U—O bond.

Positions of the oxygen atoms

The positions of the oxygen atoms were discussed from geometrical arguments without assuming any special space group. We felt it justified to assume that the O—O distances are not less than 2.6 Å and that the distances between interacting U and O atoms are within the limits 1.6—2.5 Å (cf. Zachariassen).

If none of the oxygen atoms were shared between two or more uranium atoms, the structure would be built up of separate molecules and every uranium should be surrounded by only four oxygen atoms. This is not very probable as the coordination number of U is 6—8. Moreover, crystals of UO₄(OH)₂ built up of separate molecules should be easily soluble in water, as, for instance, is H₂SO₄. The crystals are, however, very sparingly soluble in water, and from this reason too the configuration seems rather improbable. Thus it is likely that the uranium atoms are joined by oxygen (or OH⁻) bridges to form infinite chains, layers, or a three-dimensional framework, as they are in the "uranates", which are difficult to bring in solution.

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Now, every uranium atom is surrounded by four other uranium atoms at a
distance of \( 4.22 \, \text{Å} - \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2}\right)^2} \), all other U—U distances being larger than
5.63 Å.

If the oxygen atoms in the bridges were to be shared between three or more
uranium atoms, the U—O distances would be larger than 2.8 Å, i.e. too long
for a U—O interaction. We thus concluded that each of them is in contact
only with two uranium atoms.

The shared oxygen atoms (O_{II}) are then probably situated between the
uranium atoms, 4.22 Å apart, as the U—O_{II} distances would otherwise be longer
than 2.8 Å. The uranium atoms could then be joined either by double
oxygens bridges leading to the formation of chains, as in MgUO₄¹¹, or by single
oxgen bridges leading to the formation of pseudo-tetragonal layers, as in
BaUO₄¹⁰, etc.

In the first case the distances U—O_{II} would be 2.48 Å, if the oxygen atoms
were situated 2.60 Å apart. According to Zachariasen¹², this would indicate a
U—O bond strength of about 0.45 units. As there are four such bonds we
would have \( 6 - 4 \times 0.45 = 4.2 \) units left for bonds to the remaining oxygen
atoms O₁ in the coordination polyhedron, leading to the very short bond dis-
tances U—O₁ = 1.6 Å. (The shortest experimentally determined distance
U—O₁ is 1.76 Å in K₂UO₂F₈, corresponding to a bond strength of 1.63. The
distance U—O₁ = 1.58 Å in RbUO₂(NO₃)₃ was estimated and is therefore
very uncertain¹⁴.)

In the second case when the distance between the uranium atoms is 4.22 Å,
the bond distance U—O₁ would be \( \frac{1}{2} \times 4.22 \, \text{Å} = 2.11 \, \text{Å} \), corresponding
to a bond strength of about 0.95. The bond strength left for bonds to the two
remaining oxygen atoms O₁ in the coordination polyhedron would then be
2.2, giving a distance U—O₁ = 2.0 Å, which is close to those observed for the
uranyl groups in the "uranates" mentioned above.

From these considerations the second case with single oxygen bridges
seemed to be the most plausible and we concluded that the bridging oxygen
atoms are situated in the following way:

\[ 8 \text{O}_{II} \text{ in Fmmm } 8(e): (0,0,0; 0,\frac{1}{2},\frac{1}{2}; \frac{1}{2},0,\frac{1}{2}; \frac{1}{2},\frac{1}{2},0) \pm (\frac{1}{4},\frac{1}{4},0; \frac{1}{4},\frac{1}{4},\frac{1}{2}) \]

Thus the crystals contain pseudo-tetragonal layers similar to those in BaUO₄.

In all the "uranates" previously determined there are UO₂⁺ ions with U—O =
1.76—2.08 Å, and thus it is plausible that our crystals also contain uranyl
groups, perpendicular, or almost perpendicular, to the sheets. As we have
found the unit cell to contain four uranium atoms there must be eight uranyl
oxygen atoms (O₁) in addition to the eight bridging oxygen atoms (O_{II}), the
approximate positions of which we have already found. The O₁ atoms should
then be arranged as follows:

\[ 8 \text{O}_{I} \text{ in Fmmm } 8(i): (0,0,0; 0,\frac{1}{2},\frac{1}{2}; \frac{1}{2},0,\frac{1}{2}; \frac{1}{2},\frac{1}{2},0) \pm (0,0,z) \text{ with } z = 0.20 \]

The parameter \( z = 0.20 \) was determined from the distance U—O₁ = 2.0 Å
expected from the bond strength \( s = 1.1 \) in the uranyl bond (cf. above).

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In this way we have found the positions of 4 U and 16 O atoms in the unit cell, corresponding to the formula $\text{UO}_4(\text{OH})_2$, as indicated by the analysis. However, since the chemical analysis was not quite conclusive as the sample contained some impurities, and since the structure seemed to be very open we concluded to investigate whether there could be more oxygen atoms present in the unit cell.

We found then that the most favourable positions for any additional O atoms ($O_{\text{III}}$) would be at $(0,0,0; \frac{1}{4},\frac{1}{4},0; 0,\frac{1}{4},\frac{1}{4}; \frac{1}{4},0,\frac{1}{4}) \pm (\frac{1}{4},\frac{1}{4},\frac{1}{4})$. An investigation showed, however, that even if the structure would be distorted a little some O—$O_{\text{III}}$ distances came out rather short (2.4 \AA{} or less) and thus it did not seem probable that the unit cell contained any additional oxygen atoms at all. This also supports the conclusion made from the analytical data that the formula of the compound should be $\text{UO}_4(\text{OH})_2$.

Positions of the hydrogen atoms

As there are 4 O atoms per U(VI) atom electrical neutrality demands 2 H atoms per U, and thus the cell must contain 8 H. They can be situated close to the uranyl oxygen atoms ($O_1$) or close to the bridging oxygen atoms ($O_2$). From the considerations of the bond strength of the $\text{U}—O$ bond the first seems to be rather plausible as the total bond strength for $O_1$ is 1.1 when the total bond strength for $O_2$ is 1.9. On the other hand, investigations on the hydrolysis of uranyl ions\textsuperscript{15,16} show that $\text{UO}_2^{2+}$ groups do not seem to attract protons in acidic solutions, which would demand that in the crystals of $\text{UO}_4(\text{OH})_2$ we would have the hydrogen atoms situated at the $O_2$ atoms forming $\text{OH}^-$ ions.

At present we could not say which of the two possibilities is the correct one even if the argument in the second case seems to be the most convincing.

In both cases the hydrogen atoms may form hydrogen bonds to the neighbouring oxygen atoms.

Final structure proposition

We thus consider that the crystals have the following structure:

Space group: No. 69 $Fmm\bar{m}$ with

\[
\begin{align*}
(0,0,0; & \frac{1}{4},\frac{1}{4},0; \frac{1}{4},\frac{1}{4},\frac{1}{4}; \frac{1}{4},0,\frac{1}{4}) \pm \\
4 \text{ U} & \text{ in } 4(a): 0,0,0 \\
8 \text{ O}_1 & \text{ in } 8(i): 0,0,2 \text{ with } z = 0.20 \\
8 \text{ O}_2 & \text{ in } 8(e): \frac{1}{4},\frac{1}{4},0; \frac{1}{4},\frac{1}{4},\frac{1}{4}
\end{align*}
\]

DISCUSSION OF THE STRUCTURE

Projections of the structure on the $xy$ and $xz$ planes are shown in Figs. 1 and 2. The structure is built up of layers $\text{UO}_4(\text{OH})_2$ consisting of linear $\text{UO}_2^{2+}$ ions (perpendicular to the sheets) joined to each other through oxygen atoms, two uranyl ions sharing one O atom. The layers are perpendicular to the c
Fig. 1. Part of the structure of $\beta$-UO$_2$(OH)$_2$ projected on the xy plane. Only atoms with $z$ within the limits $-0.25 \leq z \leq 0.25$ have been marked out.

axis, and they are connected to each other by van der Waals forces between the uranyl groups.

The distances between the atoms in the same layer would be:

$$\begin{align*}
U -2 O_I, O_I - U &= 2.0 \ \text{Å} \\
U -4 O_{II}, O_{II} - 2 U &= 2.11 \ \text{Å} \\
O_I -4 O_{II}, O_{II} - 2 O_I &= 2.84 \ \text{Å} \\
O_{II} -4 O_{II} &= 2 \times 2.82, 2 \times 3.15 \ \text{Å}
\end{align*}$$

The layers support each other by:

$$O_I - 4 O_I = 2 \times 3.05, 2 \times 3.36 \ \text{Å}$$

These figures are all within the normal range, showing that O—O interaction also occurs in the lattice. However, the bond lengths may be inaccurate by one or a few 0.1 Å since the positions of the oxygen atoms have been inferred from geometrical arguments.

Fig. 2. The structure of $\beta$-UO$_4$(OH)$_2$ projected on the xz plane.

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During the Manhattan project Zachariasen \(^2\) made a preliminary structure determination of an orthorhombic uranyl hydroxide, \(\alpha\)-UO\(_4\)(OH)\(_2\). Its cell dimensions were found to be \(a = 6.86 \pm 0.03 \text{ Å}, b = 4.27 \pm 0.03 \text{ Å}, c = 10.19 \pm 0.06 \text{ Å}, V = 299 \text{ Å}^3\) and the phase is thus different from ours. Zachariasen determined the positions of its uranium atoms but not those of its oxygen atoms. He found that every uranium is surrounded by six others at distances 4.05—4.27 Å in pseudohexagonal layers. Zachariasen’s \(\alpha\)-UO\(_4\)(OH)\(_2\) structure then seems to resemble the hexagonal "uranates", whereas our structure is closely related to the tetragonal "uranates", where every uranium atom is surrounded by four others at the distance 4.22 Å.

In "The Chemistry of Uranium" \(^3\) four phases of UO\(_4\)(OH)\(_2\) are described. Two of them (\(\alpha\) and \(\beta\)) are said to be orthorhombic, and as Zachariasen’s crystals were called \(\alpha\)-UO\(_4\)(OH)\(_2\), the phase described in our paper should be \(\beta\)-UO\(_4\)(OH)\(_2\). However, the data are very meagre, and the identity between our crystals and the \(\beta\) phase there could not be definitely stated.

We wish to thank Professor Lars Gunnar Sillén and Dr. Arne Magnus for many valuable discussions in connection with this work. We are also very much indebted to Professor Gustaf Ljunggren, FOA 1, and Professor Arne Ölander, University of Stockholm, for their kind interest.

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