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X-Ray Investigations on Uranyl Hydroxides

I. The Crystal Structure of β-$UO_2(OH)_2$

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β-$UO_2(OH)_2$ has a face-centered orthorhombic cell with the dimensions $a = 6.295 \pm 0.005$ Å, $b = 5.636 \pm 0.005$ Å, and $c = 9.92_9 \pm 0.01$ 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_2^{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.* α-$UO_2(OH)_2$, 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 [2] are mainly concerned with the identification of different phases of $UO_2(OH)_2(H_2O)_x$. 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 β-$UO_2(OH)_2$ 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 $UO_2(CH_3COO)_2$ 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 focussing 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 $\sin^2\Theta$ 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-$UO_2(OH)_2$ [2], 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 [5]. 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 U_3O_8. The water was determined by Brush [6] and Penfield's [7] method, described by Kolthoff and Sandell [8].

	Found		Calculated for $UO_2(OH)_2$
% UO_3	93.0	93.2	94.08
% H_2O	5.9	6.1	5.92
Density	5.72	5.72	5.73

The analyses indicate the formula $UO_2(OH)_2$. 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 $UO_2(OH)_2$.

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: $a = 6.2_9$ Å, $b = 5.6_3$ Å, and $c = 9.9_3$ Å. 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:

$$\begin{aligned} a &= 6.295 \pm 0.005 \text{ Å} \\ b &= 5.636 \pm 0.005 \text{ Å} \\ c &= 9.92_9 \pm 0.01 \text{ Å} \\ V &= 352.4 \text{ Å}^3 \end{aligned}$$

All reflections hkl with $h + k =$ odd or $k + l =$ odd are systematically absent. This is characteristic of the space groups No. 69 $Fmmm$, No. 42

Table 1. Powder photographs of β-$UO_2(OH)_2$. *CrK radiation* $\lambda_{CrK\alpha} = 2.2909$ Å.

h k l	$10^4\sin^2\Theta$ calc	$10^4\sin^2\Theta$ obs	*I* obs	*h k l*	$10^4\sin^2\Theta$ calc	$10^4\sin^2\Theta$ obs	*I* obs
1 1 1	877	870	m	4 0 0	5298	5297	vw
—	—	962	vw	—	—	5658	vvw
—	—	1125	w	4 0 2	5831	5844	vw
2 0 0	1324	1323	w	2 0 6	6118	6121	m
—	—	1493	vvw	—	—	6209	w
0 2 0	1652	(1642)	w	—	—	6296	w
2 0 2	1857	1851	vw	0 2 6	6446	(6443)	w+
1 1 3	1943	1933	w	0 4 0	6608	(6607)	vw
—	—	1969	w—	3 1 5	6722	6725	w
—	—	1981	m	3 3 1	6830	6822	w
0 0 4	2131	2129	m	4 2 0	6950	6957	vvw
0 2 2	2185	2182	vw—	0 4 2	7141	—	—
—	—	2924	vw	1 1 7	7269	7262	s
2 2 0	2976	2983	vw—	1 3 5	7377	7377	vw
—	—	3070	vw	4 0 4	7429	7440	w
—	—	3218	vw	4 2 2	7483	—	—
—	—	3307	vw	2 2 6	7780	7771	w+
2 0 4	3455	3457	w+	3 3 3	7896	7884	vvw
2 2 2	3509	3519	vw	2 4 0	7932	—	—
3 1 1	3526	3534	vw	—	—	7963	w+
0 2 4	3783	3782	w—	—	—	8150	w
—	—	3893	vvw	—	—	8228	w
1 1 5	4073	4068	s	—	—	8418	w
1 3 1	4181	4186	vvw	2 4 2	8465	—	—
—	—	4290	w	0 0 8	8523	8511	m
—	—	4433	w—	0 4 4	8739	8740	vw—
—	—	4492	m	5 1 1	8824	8837	vvw
3 1 3	4592	4597	vw	—	—	9051	vvw
0 0 6	4794	4789	m	4 2 4	9081	9082	vw—
2 2 4	5107	5098	vw	—	—	9533	vw
1 3 3	5245	5248	vw	—	—	9686	vw

The horizontal lines mark the boundaries between the angular ranges of the three different focussing cameras used. Reflections systematically absent in the space group *Fmmm* have been omitted. Reflections coinciding with β reflections are given in brackets. Reflections having no corresponding $\sin^2\Theta$ 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.

*Fmm*2, and No. 22 *F*222. 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 Θ.

Positions of the uranium atoms

The plausible space groups demand that there should be 4*n* uranium atoms in the unit cell (where *n* is an integer). From the volume of the cell we can calculate that, for $n = 1$, $d_{\text{calc}} = 5.73$ (assuming the formula as $UO_2(OH)_2$). 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

4 U atoms per unit cell. We may arbitrarily choose their positions as 4(*a*) in *Fmmm*, 4(*a*) in *F*222 or 4(*a*) with $z = 0$ in *Fmm*2. All these positions have the coordinates 000; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$, 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 α-UO_3, seem to contain uranyl ions UO_2^{2+}. In the "uranates" investigated ($CaUO_4$, $SrUO_4$, $BaUO_4$, Li_2UO_4, Na_2UO_4, K_2UO_4, $MgUO_4$) [9-11], the uranium atoms are connected by oxygen bridges forming $(UO_2O_2)_n^{2n-}$-layers or chains perpendicular, or almost perpendicular, to the uranyl groups.

In $BaUO_4$ and $MgUO_4$ each oxygen bridge connects two neighbouring uranyl groups, resulting in pseudo-tetragonal $(UO_2O_2)_n^{2n-}$-layers with single oxygen bridges for $BaUO_4$ [10] and $(UO_2O_2)_n^{2n-}$-chains with double oxygen bridges for $MgUO_4$.[11] The distances U—O_{bridge} are 2.12—2.22 Å.

In the other "uranates" mentioned each UO_2^{2+} group is connected with its next six UO_2^{2+} 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—O_{bridge} are 2.3 Å.

In α-UO_3 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 UO_2^{2+} groups.

A compilation of all observed U—O distances has been given by Zachariasen [12]. 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.* Zachariasen [12]).

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 $UO_2(OH)_2$ built up of separate molecules should be easily soluble in water, as, for instance, is H_2SO_4. 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.

Now, every uranium atom is surrounded by four other uranium atoms at a distance of 4.22 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 oxygen bridges leading to the formation of chains, as in $MgUO_4$[11], or by single oxygen bridges leading to the formation of pseudo-tetragonal layers, as in $BaUO_4$[10].

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 Zachariasen[12], 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 O_I in the coordination polyhedron, leading to the very short bond distances U—O_I = 1.6 Å. (The shortest experimentally determined[13] distance U—O_I is 1.76 Å in $K_3UO_2F_5$ corresponding to a bond strength of 1.63. The distance U—O_I = 1.58 Å in $RbUO_2(NO_3)_3$ was estimated and is therefore very uncertain[14].)

In the second case when the uranium atoms are joined by single oxygen bridges the distance U—O_{II} would be $\frac{1}{2} \times 4.22$ Å $= 2.11$ Å corresponding to a bond strength of about 0.95. The bond strength left for bonds to the two remaining oxygen atoms O_I in the coordination polyhedron would then be 2.2, giving a distance U—O_I = 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 O_{II} in *Fmmm* 8(*e*): $(0,0,0;\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},0,\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},0) \pm (\tfrac{1}{4},\tfrac{1}{4},0;\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{2})$

Thus the crystals contain pseudo-tetragonal layers similar to those in $BaUO_4$.

In all the "uranates" previously determined there are UO_2^{2+} 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 (O_I) in addition to the eight bridging oxygen atoms (O_{II}), the approximate positions of which we have already found. The O_I atoms should then be arranged as follows:

8 O_I in *Fmmm* 8(*i*): $(0,0,0;\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},0,\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},0) \pm (0,0,z)$ with $z = 0.20$

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

In this way we have found the positions of 4 U and 16 O atoms in the unit cell, corresponding to the formula $UO_2(OH)_2$, 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_{III}) would be at $(0,0,0;\ \frac{1}{2},\frac{1}{2},0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2})\ \pm(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. An investigation showed, however, that even if the structure would be distorted a little some $O—O_{III}$ distances came out rather short (2.4 Å 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 $UO_2(OH)_2$

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_I) or close to the bridging oxygen atoms (O_{II}). From the considerations of the bond strength of the U—O bond the first seems to be rather plausible as the total bond strength for O_I is 1.1 when the total bond strength for O_{II} is 1.9. On the other hand, investigations on the hydrolysis of uranyl ions [15,16] show that UO_2^{2+} groups do not seem to attract protons in acidic solutions, which would demand that in the crystals of $UO_2(OH)_2$ we would have the hydrogen atoms situated at the O_{II} atoms forming 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 *Fmmm* with

$(0,0,0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0)\ \pm$

4 U	in 4(*a*):	0,0,0
8 O_I	in 8(*i*):	$0,0,z$ with $z = 0.20$
8 O_{II}	in 8(*e*):	$\frac{1}{4},\frac{1}{4},0;\frac{1}{4},\frac{1}{4},\frac{1}{2}$

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 $UO_2(OH)_2$ consisting of linear 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*

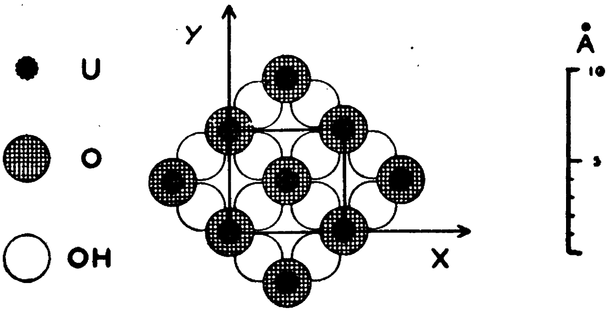

Fig. 1. Part of the structure of β-$UO_2(OH)_2$ *projected on the* xy *plane. Only atoms with* z *within the limits* $-0.25 \leq z \leq 0.25$ *have been marked out.*

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:

$$\begin{array}{ll} U - 2\,O_I,\ O_I - U & = 2.0\ \text{Å} \\ U - 4\,O_{II},\ O_{II} - 2\,U & = 2.11\ \text{Å} \\ O_I - 4\,O_{II},\ O_{II} - 2\,O_I & = 2.8_4\ \text{Å} \\ O_{II} - 4\,O_{II} & = 2 \times 2.82,\ 2 \times 3.15\ \text{Å} \end{array}$$

The layers support each other by:

$$O_I - 4\,O_I = 2 \times 3.0_5,\ 2 \times 3.3_6\ \text{Å}$$

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.

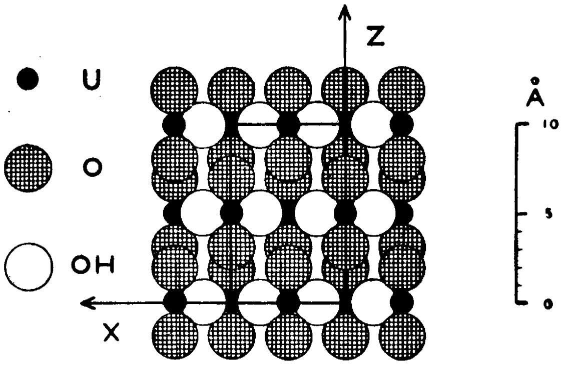

Fig. 2. The structure of β-$UO_2(OH)_2$ *projected on the* xz *plane.*

During the Manhattan project Zachariasen[2] made a preliminary structure determination of an orthorhombic uranyl hydroxide, α-$UO_2(OH)_2$. Its cell dimensions were found to be $a = 6.86 \pm 0.03$ Å, $b = 4.27 \pm 0.03$ Å, $c = 10.19 \pm 0.06$ Å, $V = 299$ 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 α-$UO_2(OH)_2$ 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"*[2] four phases of $UO_2(OH)_2$ are described. Two of them (α and β) are said to be orthorhombic, and as Zachariasen's crystals were called α-$UO_2(OH)_2$, the phase described in our paper should be β-$UO_2(OH)_2$. However, the data are very meagre, and the identity between our crystals and the β phase there could not be definitely stated.

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