Acta Cryst. (1954). **7**, 788

Crystal Chemical Studies of the 5*f*-Series of Elements. XXI. The Crystal Structure of Magnesium Orthouranate

By W. H. Zachariasen

Argonne National Laboratory and Department of Physics, University of Chicago, Chicago, Illinois, U.S.A.

(*Received* 23 *July* 1954)

Magnesium orthouranate, $Mg(UO_2)_2$, is found to be orthorhombic body-centered with four stoichiometric molecules in a unit cell of dimensions $a_1 = 6{\cdot}520$ Å, $a_2 = 6{\cdot}595$ Å, $a_3 = 6{\cdot}924$ Å. The space group is *Iman*.

The structure is of a type not previously encountered for orthouranates, containing endless chains UO_2O_2 rather than the endless layers hitherto observed.

The structure contains collinear uranyl groups with U–O = 1·92±0·03 Å. Uranium forms four secondary U–O bonds in the plane normal to the uranyl group, these bond lengths being 2·16±0·03 Å and 2·20±0·03 Å. The six oxygen atoms about each uranium atom form a distorted octahedron, and these octahedra share edges with one another to form endless chains UO_2O_2 parallel to the a_3 axis. The orthouranate chains are linked together by the magnesium atoms, each magnesium atom being bonded to six oxygen atoms belonging to four different chains. The Mg–O bond lengths are 1·98±0·01 Å (twice) and 2·19±0·02 Å (four times).

Introduction

Because of the unfavorable situation as to atomic scattering power and excessive absorption, the structural results reported in the literature for uranyl compounds leave much to be desired as regards the accuracy with which the light atoms have been located. In a few instances the positions of the light atoms have been directly determined from the intensity data, but the limits of error have been quite considerable. In all other cases positions have been assigned to the light atoms on the basis of spatial considerations.

In view of this unsatisfactory state of affairs the writer has undertaken a series of structural studies of uranyl compounds. With the aid of accurate intensity measurements and precise evaluation of absorption corrections it is possible to get reliable structural information so essential to a thorough understanding of the crystal chemistry of the class of compounds under consideration. This paper gives the results of the second investigation of the series, the crystal structure of $K_3UO_2F_5$ having been reported on in the first paper.

Cell dimensions

Minute, orange-brown crystal needles of $MgUO_2O_2$ were prepared by adding U_3O_8 to a melt of $MgCl_2$ (Ditte, 1884). The formation of the uranate is by slow hydrolysis of the chloride. The needles were found to be orthorhombic. The needle axis was chosen as the [001] direction, the prominent faces being (100) and (010).

The unit cell dimensions are

$$a_1 = 6{\cdot}520 \pm 0{\cdot}002,\ a_2 = 6{\cdot}595 \pm 0{\cdot}002,\ a_3 = 6{\cdot}924 \pm 0{\cdot}002 \text{ Å},$$

with four molecules per unit cell. The calculated density is $\varrho = 7{\cdot}28$ g.cm.$^{-3}$.

The great majority of the crystal needles were found to be twinned. The [001] direction is common to the two individuals, but the (100) plane of one individual coincides with the (010) plane of the other.

The structure determination is based upon intensity measurements made with the XRD Spectrometer modified for single-crystal work as described in a recent article (Zachariasen, 1954*a*). Unfortunately the crystals were too small to be successfully ground into cylindrical or spherical shape to simplify the absorption correction. The crystal used in the investigation was an orthogonal parallelopiped of linear dimensions $1{\cdot}15 \times 10^{-3}$ cm., $2{\cdot}30 \times 10^{-3}$ cm. and $34{\cdot}7 \times 10^{-3}$ cm. along the three directions $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. All reflections in the four layer lines $H_3 = 0, 1, 2$ and 3 were measured using Cu $K\alpha$ radiation.

The linear absorption coefficient is $1{\cdot}90 \times 10^3$ cm.$^{-1}$. Hence the absorption correction is very large in spite of the small transverse dimensions of the crystal. The simple geometrical shape of the crystal made it possible to evaluate the absorption correction by means of straight forward but tedious direct integration. However, these integrations were carried out without approximation only for the H_1H_20 reflections. For reflections $H_1H_2H_3$ in other layers lines the absorption correction was evaluated as if $H_3 = 0$, and then a small correction was applied to allow for the small increase in path length as compared with the corresponding zero-layer reflections.

Determination of the structure

The translation lattice is body-centered, and reflections H_10H_3 are absent unless H_1 and H_3 are both even. Accordingly, the space group symmetry is likely to be *Iman* or *Ima*. The holohedral group *Iman* was assumed to be the correct one, and this assumption proved to be valid.

Table 1. *Observed and calculated structure factors for* H_1H_20 *and* H_1H_22

	$H_3 = 0$		$H_3 = 2$	
H_1H_2	F_c	F_o	F_c	F_o
11	68	60	74	73
02	82	80	74	78
20	85	77	41	45
22	58	57	53	55
13	44	44	68	70
31	67	66	72	74
04	68	65	45	46
40	78	72	46	46
33	46	45	66	63
24	57	53	33	37
42	58	58	53	54
15	38	38	37	36
51	41	41	47	46
44	50	52	35	40
35	38	40	38	39
53	29	32	45	46
06	40	39	28	24
60	55	53	36	37
26	32	33	20	20
62	44	41	39	39
17	15	15	27	24
55	28	33	27	33
71	40	39	44	40
46	31	32	21	21
64	37	36	28	27
37	16	16	27	26
73	30	30	41	39
08	19	16	16	15
80	40	38		
28	14	13		
82	32	29		

Table 2. *Observed and calculated structure factors for* H_1H_21 *and* H_1H_23

	$H_3 = 1$		$H_3 = 3$	
H_1H_2	F_c	F_o	F_c	F_o
01	11	16		
12	19	20	18	20
21	8	8	11	12
03	31	33	26	26
23	23	24	20	20
32	18	18	18	19
14	30	32	25	25
41	9	8	9	9
05	36	37	33	30
34	30	32	26	27
43	22	22	19	20
25	28	30	26	26
52	12	13	12	12
16	32	31	31	27
61	6	6	7	7
45	28	30	26	28
54	20	22	18	20
36	32	32	32	29
63	18	18	16	16
07	35	33	35	33
27	28	28	28	31
72	11	12	11	12
56	23	23		
65	22	22		
18	30	30		
47	29	27		
74	20	20		
81	4	5		

It is readily seen from the experimentally determined structure factors (Tables 1 and 2) that the uranium atoms are in positions

$$4(e)\colon\ \pm(0, y, \tfrac{1}{4})\,.$$

The parameter y could be determined with high accuracy without knowing the whereabouts of the magnesium and oxygen atoms, the result being $y = 0{\cdot}0222 \pm 0{\cdot}0010$. In calculating the uranium contribution to the structure factor the uranium scattering power was taken to be $(f-\Delta)\exp\left[-0{\cdot}45\sin^2\theta/\lambda^2\right]$, where f represents the values given in the *International Tables*. Δ is the anomalous dispersion correction representing the sum of the K and L oscillator strengths, which, according to Hönl, are 1·12 and 4·50, respectively, so that $\Delta = 5{\cdot}6$. The slight dependence of Δ on $\sin\theta/\lambda$ was neglected. The experimentally determined temperature factor corresponds to a root mean square amplitude of 0·075 Å at room temperature. There was no indication of a significant amount of anisotropy in the heat motion. In view of the large uranium contribution the algebraic signs of all structure factors are determined, and it hence becomes possible to find the magnesium and oxygen positions in direct manner by means of suitable Fourier syntheses.

In order to minimize the termination-of-series error it is convenient to eliminate the uranium atoms for which the positions are known. The data being restricted to the layer lines $H_3 = 0, 1, 2$ and 3, and there being reflection planes at $z = \pm\frac{1}{4}$, the most general form of Fourier synthesis which can be evaluated is

$$\tfrac{1}{2}V\int_0^1(\varrho-\varrho_\mu)\left(1+C_1\sin 2\pi z+C_2\cos 2\pi 2z+C_3\sin 2\pi 3z\right)dz.$$

Two such generalized projections were evaluated, namely $C_1 = 1$ and $C_2 = C_3 = \pm 1$. The coefficients of the resulting double Fourier series are $F_{H_1H_20} \pm F_{H_1H_22}$ for the cosine terms and $-F_{H_1H_21} \mp F_{H_1H_23}$ for the sine terms, where $F_{H_1H_2H_3}$ represents the structure-factor contribution of magnesium and oxygen atoms. The choice $C_2 = C_3 = -1$ serves to enhance the atoms lying in the reflection plane $z = \frac{1}{4}$. For $C_2 = C_3 = +1$ the atoms in the reflection planes are suppressed while those with $z \approx 0$ are enhanced.

Fig. 1 shows the generalized projection corresponding to $C_1 = 1$, $C_2 = C_3 = -1$. Accordingly there is one set of eight oxygen atoms in positions

$$8(i)\colon\ \pm(x, y, \tfrac{1}{4}),\ (\bar{x}, y, \tfrac{1}{4})\,.$$

The position of the peak in Fig. 1 corresponds to $x = 0{\cdot}295 \pm 0{\cdot}003$, $y = 0{\cdot}022 \pm 0{\cdot}003$. The generalized projection with $C_1 = C_2 = C_3 = +1$ reveals that the eight remaining oxygen atoms are in positions

$$8(h)\colon\ \pm(0, y, z),\ (0, y, \tfrac{1}{2}-z)$$

and that the four magnesium atoms are in positions

$$4(b)\colon\ (0, \tfrac{1}{2}, 0),\ (0, \tfrac{1}{2}, \tfrac{1}{2})\,.$$

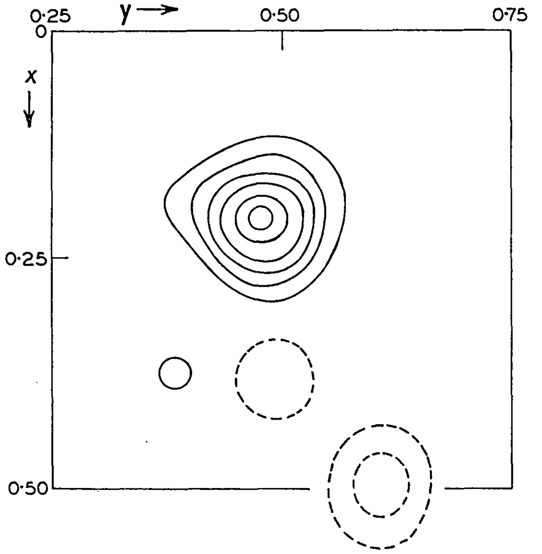

Fig. 1. The generalized projection corresponding to $C_1 = 1$, $C_2 = C_3 = -1$ which enhances atoms at $z = \frac{1}{4}$ and suppresses atoms at $z = 0$. This is a difference synthesis, the uranium atom having been removed. Broken contours indicate negative electron density.

The generalized projection evaluated along the direction $x = 0$ is shown in Fig. 2. The highest peak is due to the magnesium atoms at $(0, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$, the two other peaks at $y = \pm 0{\cdot}200 \pm 0{\cdot}004$ being due to oxygen atoms. The oxygen peak at $y = -0{\cdot}200$ is higher than that at $y = +0{\cdot}200$, the ratio of the peak heights being 1·35. This ratio should equal the ratio of the weight function $1+\sin 2\pi z+\cos 2\pi 2z+\sin 2\pi 3z$ at $-z$ and z, and thus gives $z = -0{\cdot}012 \pm 0{\cdot}004$.

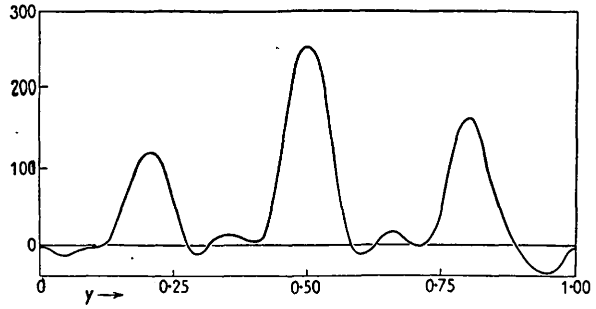

Fig. 2. The generalized difference synthesis corresponding to $C_1 = C_2 = C_3 = 1$ evaluated along the direction $x = 0$. The high peak at $y = \frac{1}{2}$ is due to magnesium, while oxygen (O_{II}) atoms are at $y = \pm 0{\cdot}20$.

The following structure has thus been obtained:
Space group: *Iman*.
Atomic positions: $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$

$$\begin{aligned}
&4\,\mathrm{U} \text{ in } 4(e)\colon\ \pm(0, y, \tfrac{1}{4}) \text{ with } && y = 0{\cdot}0222 \pm 0{\cdot}0010;\\
&4\,\mathrm{Mg} \text{ in } 4(b)\colon\ (0, \tfrac{1}{2}, 0),\ (0, \tfrac{1}{2}, \tfrac{1}{2});\\
&8\,\mathrm{O_I} \text{ in } 8(i)\colon\ \pm(x, y, \tfrac{1}{4}),\ (\bar{x}, y, \tfrac{1}{4}) \text{ with } && x = 0{\cdot}295 \pm 0{\cdot}003,\\
& && y = 0{\cdot}022 \pm 0{\cdot}003;\\
&8\,\mathrm{O_{II}} \text{ in } 8(h)\colon\ \pm(0, y, z),\ (0, y, \tfrac{1}{2}-z) \text{ with } && y = 0{\cdot}200 \pm 0{\cdot}004,\\
& && z = -0{\cdot}012 \pm 0{\cdot}004.
\end{aligned}$$

Observed and calculated structure factors are compared in Tables 1 and 2.

Discussion of the structure

A view of the structure along $\mathbf{a}_1$ is shown in Fig. 3. Shown are only the uranium and magnesium atoms at $x = 0$ and the oxygen atoms to which they are bonded.

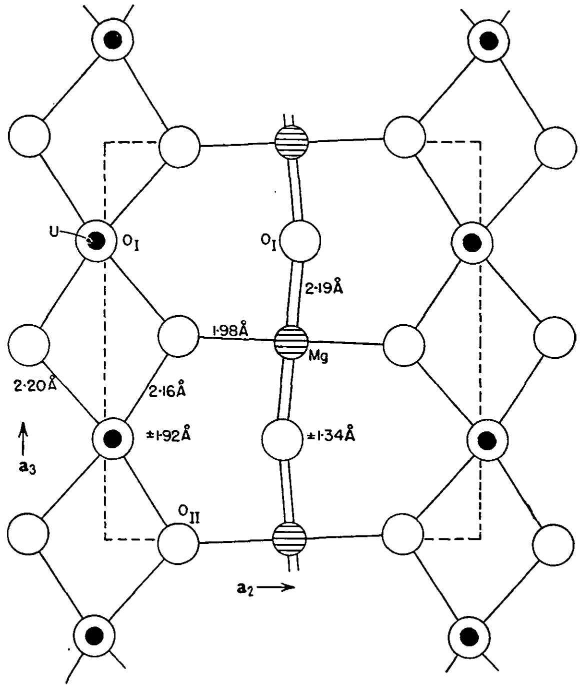

Fig. 3. View of the structure along $\mathbf{a}_1$. Magnesium and uranium atoms at $x = \frac{1}{2}$ and their neighboring oxygen atoms have been removed so that the structure of the orthouranate chains along $\mathbf{a}_3$ can be better demonstrated.

The structure contains uranyl groups O_I–U–O_I. These groups are collinear within experimental error, and it should be emphasized that collinearity is not required by the space-group symmetry. The uranyl group is parallel with $\mathbf{a}_1$, and the bond length is $\mathrm{U{-}O_I} = 1{\cdot}92\pm0{\cdot}03$ Å. This result agrees well with the less accurate value of $1{\cdot}91\pm0{\cdot}10$ Å found in the $\mathrm{Ca(UO_2)O_2}$ structure (Zachariasen, 1948), but is considerably larger than the bond length of $1{\cdot}76\pm0{\cdot}03$ Å observed in the compound $\mathrm{K_3UO_2F_5}$ (Zachariasen, 1954*b*). An explanation for the observed wide variation in the uranyl bond length has been offered in a recent article (Zachariasen, 1954*b*).

Each uranium atom is bonded to two uranyl oxygens ($\mathrm{O_I}$) and to four other oxygens ($\mathrm{O_{II}}$), while each magnesium atom is bonded to four $\mathrm{O_I}$ and to two $\mathrm{O_{II}}$ atoms. The individual distances are:

$\mathrm{U{-}2\,O_I}$	$1{\cdot}92\pm0{\cdot}03$ Å	$\mathrm{Mg{-}4\,O_I}$	$2{\cdot}19\pm0{\cdot}02$ Å
$\mathrm{-2\,O_{II}}$	$2{\cdot}16\pm0{\cdot}03$	$\mathrm{-2\,O_{II}}$	$1{\cdot}98\pm0{\cdot}01$
$\mathrm{-2\,O_{II}}$	$2{\cdot}20\pm0{\cdot}03$		

The four $\mathrm{U{-}O_{II}}$ bonds are normal to the uranyl bonds, the two $\mathrm{O_I}$ and the four $\mathrm{O_{II}}$ atoms forming a distorted octahedron about the uranium atom. The atomic configuration about uranium is quite similar to the one suggested by spatial considerations in the $\mathrm{Ba(UO_2)O_2}$ structure (Samson & Sillén, 1947).

As seen in Fig. 3, the distorted $\mathrm{(UO_2)O_4}$ octahedra share edges to form endless chains of average composition $\mathrm{(UO_2O_2)}$ parallel with $\mathbf{a}_3$, which is the needle axis of the crystals. The shared $\mathrm{O_{II}{-}O_{II}}$ edge is 2·64 Å, while the unshared $\mathrm{O_{II}{-}O_{II}}$ octahedral edges are 3·29 Å and 3·61 Å. The chains are linked together by means of the magnesium atoms, the six Mg–O bonds going to four different chains. The distorted $\mathrm{MgO_6}$ octahedra also share edges with one another so as to form endless chains parallel to the needle axis. Indeed, these magnesium–oxygen chains are remarkably similar to the uranium–oxygen chains. Even the uranyl group is simulated by the short $\mathrm{O_{II}{-}Mg{-}O_{II}}$ axis of the $\mathrm{MgO_6}$ octahedron, which is parallel with $\mathbf{a}_2$ whereas the uranyl group is parallel with $\mathbf{a}_1$. It is this remarkable similarity between the two sets of chains which is responsible for the observed twinning.

All other orthouranates so far investigated are layer structures with the uranyl groups normal to the layers. The uranium atom forms six secondary $\mathrm{U{-}O_{II}}$ bonds in the orthouranates of calcium and strontium (Zachariasen, 1948) and of potassium, sodium and lithium (Zachariasen, 1945), and the $\mathrm{UO_2O_6}$ polyhedra are bonded together to form endless hexagonal or pseudohexagonal layers. In the $\mathrm{Ba(UO_2)O_2}$ structure uranium forms, according to Samson & Sillén, only four secondary $\mathrm{U{-}O_{II}}$ bonds, and the resulting $\mathrm{UO_2O_4}$ octahedra share only corners to give endless pseudotetragonal layers. (The two types of layers are depicted in Figs. 2 and 3 of paper No. IV of the present series (Zachariasen, 1948).) The previous work suggested that the presence of endless layers $\mathrm{(UO_2)O_2}$ of one or the other type was a characteristic feature of all orthouranate structures. It is therefore of interest to learn from the present investigation that chain structures may also occur.

The anhydrous magnesium chloride used in the chemical preparations was kindly furnished by Dr B. T. Matthias. Miss Anne Plettinger gave valuable aid by making some of the intensity measurements.

References

Ditte, A. (1884). *Ann. Chim.* (*Phys.*) (6), **1**, 355.

Samson, S. & Sillén, S. G. (1947). *Ark. Kemi Min. Geol.* **25**, No. 21.

Zachariasen, W. H. (1945). Manhattan Project Report CP-2611.

Zachariasen, W. H. (1948). *Acta Cryst.* **1**, 281.

Zachariasen, W. H. (1954*a*). *Acta Cryst.* **7**, 305.

Zachariasen, W. H. (1954*b*). *Acta Cryst.* **7**, 783.