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The Crystal Structure of Uranyl Dihydroxide, $UO_2(OH)_2$*

By R. B. Roof, Jr., Don T. Cromer and Allen C. Larson

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.

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As a result of single-crystal structure analysis, the material usually designated as uranium trioxide with one molecule of water of hydration, $UO_3.H_2O$, should be described chemically as uranyl dihydroxide, $UO_2(OH)_2$. The orthorhombic unit cell has the dimensions

$$a = 5{\cdot}635 \pm 0{\cdot}007,\ b = 6{\cdot}285 \pm 0{\cdot}008 \text{ and } c = 9{\cdot}919 \pm 0{\cdot}008 \text{ Å}.$$

There are four formula units per unit cell and the space group was uniquely determined from the systematic extinctions to be *Pbca*. In the least-squares refinement of the structure, a secondary extinction parameter, real and imaginary portions of the anomalous dispersion, and anisotropic thermal parameters were used. The structure can be described as composed of layers that are hydrogen-bonded together, the hydrogen-bond distance being 2·69 Å. The layers are constructed by octahedra which share corners in order to build and expand the layer. Each octahedron contains a central uranium atom, two uranyl oxygen atoms and four hydroxyl oxygen atoms.

Introduction

Dawson, Wait, Alcock & Chilton (1956) have described uranium trioxide with one molecule of water of hydration, $UO_3.H_2O$, as orthorhombic, space group *Pbca*. Their conclusion was based on the observation of several rather weak reflections. The present work confirms this space group and determines and refines the structure of the same material, which can best be described chemically as uranyl dihydroxide, $UO_2(OH)_2$. The crystals used for the structure determination were obtained as a by-product of experiments involving the oxidation of UO_2 in oxygenated water at temperatures above 200 °C. (Results of similar experiments conducted at lower temperatures and descriptions of the experimental equipment used, are given by Aronson (1958) and by Belle (1961).)

Crystallographic data

The single crystals were quite large, having an average diameter of about 200 microns, and attempts to reduce their size were unsuccessful. Cleavage perpendicular to the c axis occurs quite readily and grinding of the crystals causes them to shatter.

For $UO_2(OH)_2$ we find (Mo $K\alpha_1 = 0{\cdot}70926$ Å)

$$\begin{gathered} a = 5{\cdot}635 \pm 0{\cdot}007 \text{ Å} \\ b = 6{\cdot}285 \pm 0{\cdot}008 \\ c = 9{\cdot}919 \pm 0{\cdot}008 \\ V = 351{\cdot}3 \text{ Å}^3 \qquad Z = 4 \\ D_m = 5{\cdot}68 \text{ g.cm}^{-3} \qquad D_x = 5{\cdot}71 \text{ g.cm}^{-3} \end{gathered}$$

and space group *Pbca*, which is uniquely determined from the systematic extinctions $hk0$ absent h odd, $0kl$ absent k odd, and $h0l$ absent l odd. The linear absorption coefficient for Mo $K\alpha$ radiation is 565 cm^{-1} and the crystal used had an average radius of approximately 0·01 cm.

With $Z = 4$ there must be 4 uranium atoms and 16 oxygen atoms placed in the unit cell. Space group *Pbca* has two positional sets in which 4 uranium atoms may be placed, and we choose set 4(a). If the chemical formula were $UO_3.H_2O$, then 4 oxygen atoms could be placed in set 4(b), eight oxygen atoms in set 4(c) and the remaining 4 oxygen atoms in another fourfold set. In space group *Pbca*, however, there are no more fourfold sets in which these atoms can be accommodated. We conclude, then, that the sixteen oxygen atoms are split into two groups of eight, each group being placed in general set 8(c). Each group of eight is crystallographically and chemically distinct and, therefore, the chemical formula must be written as $UO_2(OH)_2$.

Experimental

Intensity measurements for reflections with $2\theta \leq 55°$ were made with a single-crystal orienter on an XRD 5 apparatus. Mo $K\alpha$ radiation and balanced filters were used. Since the entire hemisphere of the reciprocal lattice was investigated, most reflections were measured four times. Lorentz and polarization corrections were made in the usual manner. The intensities were also corrected for the effects of absorption. A program to calculate these corrections, which had been written by Burnham (1962) for Weissenberg geometry, was modified for single-crystal orienter geometry and incorporated into our data processing programs. After correction for absorption, equivalent reflections were averaged. An R index formed by comparing individual values of equivalent reflections with their mean values was 7·4% based on F and 14·8% based on F^2.

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There were 178 non-equivalent reflections observed out of a possible 395.

Determination of the structure

After placing 4 uranium atoms in set 4(*a*) of space group *Pbca*, difference Fourier syntheses were used to locate the oxygen atom positions at approximately $x=0{\cdot}15$, $y=0{\cdot}45$, $z=0{\cdot}35$ for the uranyl oxygen and $x=0{\cdot}20$, $y=0{\cdot}25$, $z=0{\cdot}10$ for the hydroxyl oxygen. This structure refined readily by the least-squares technique. Atomic form factors were used in the functional form given by Forsyth & Wells (1959). In all least-squares calculations, the function minimized was $\Sigma w(\Delta F)^2$ and unit weights were used.

In addition to the usual positional and thermal parameters, a secondary extinction correction was included. The least-squares program was further altered so that $\Delta f''$, the imaginary portion of the anomalous dispersion correction, could be included in the calculated structure factors. This procedure was found necessary in the determination of the structure of $UMoC_2$ (Cromer, Larson & Roof, 1964) and UF_4 (Larson, Roof & Cromer, 1964) in order to obtain positive isotropic thermal parameters.

Negative isotropic thermal parameters were not encountered in the present structure determination. However, only when g, the secondary extinction correction, and $\Delta f''$ are included in the observational equations can physically plausible anisotropic thermal parameters be obtained.

For uranium a value of $\Delta f'=-20{\cdot}0$ and $\Delta f''=+13{\cdot}0$ electrons (Roof, 1961) was used in the least-squares refinement. Anistropic thermal parameters of the form

$$\exp\,(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$$

were also employed. The final least-squares parameters are given in Table 1. The final changes as fractions of their standard deviations were $<5\times10^{-3}$ for position parameters, $<8\times10^{-3}$ for temperature factors, and $<4\times10^{-3}$ for g. Observed and calculated structure factors, for which $R=9{\cdot}7\%$, are given in Table 2.

Table 1. *Final least-squares parameters for* $UO_2(OH)_2$

The uranium atoms were corrected for the effects of anomalous dispersion with $\Delta f'=-20{\cdot}0$ and $\Delta f''=+13{\cdot}0$. The secondary extinction coefficient $g=(5{\cdot}87\pm0{\cdot}78)\times10^{-7}$

Atom	Positional parameters	Thermal parameters
U	$x=0$	$B_{11}=0{\cdot}0041\pm0{\cdot}0009$
	$y=0$	$B_{22}=0{\cdot}0116\pm0{\cdot}0009$
	$z=0$	$B_{33}=0{\cdot}0047\pm0{\cdot}0004$
		$B_{12}=0{\cdot}0039\pm0{\cdot}0056$
		$B_{13}=0{\cdot}0037\pm0{\cdot}0029$
		$B_{23}=0{\cdot}0066\pm0{\cdot}0014$
O(1)	$x=0{\cdot}1370\pm0{\cdot}0090$	$B_{11}=0{\cdot}0218\pm0{\cdot}0198$
(Uranyl)	$y=0{\cdot}4672\pm0{\cdot}0189$	$B_{22}=0{\cdot}1259\pm0{\cdot}0514$
	$z=0{\cdot}3348\pm0{\cdot}0049$	$B_{33}=0{\cdot}0025\pm0{\cdot}0041$
		$B_{12}=0{\cdot}0964\pm0{\cdot}0732$
		$B_{13}=-0{\cdot}0032\pm0{\cdot}0173$
		$B_{23}=-0{\cdot}0194\pm0{\cdot}0313$
O(2)	$x=0{\cdot}1848\pm0{\cdot}0094$	$B_{11}=0{\cdot}0288\pm0{\cdot}0206$
(Hydroxide)	$y=0{\cdot}2791\pm0{\cdot}0087$	$B_{22}=0{\cdot}0197\pm0{\cdot}0157$
	$z=0{\cdot}0925\pm0{\cdot}0047$	$B_{33}=0{\cdot}0043\pm0{\cdot}0040$
		$B_{12}=0{\cdot}0320\pm0{\cdot}0361$
		$B_{13}=-0{\cdot}0059\pm0{\cdot}0183$
		$B_{23}=0{\cdot}0063\pm0{\cdot}0151$

Discussion of the structure

Interatomic distances are listed in Table 3. The standard deviations given in this table have been computed with all correlation terms obtained from the least-squares matrix included. According to the definition of neighbor given by Cromer *et al.* (1964), U has 2 O(1) and 4 O(2) atoms as neighbors. These 6 atoms are octahedrally coordinated and form a polyhedron with 8 three-sided faces. O(1) has 4 O(1), 6 O(2) and 1 U atom as neighbors. These 11 atoms form a polyhedron with 16 three-sided faces and 1 four-sided face. O(2) has 6 O(1), 3 O(2) and 2 U atoms as neighbors. These 11 atoms form a polyhedron with 12 three-sided faces and 3 four-sided faces.

As opposed to packing by polyhedra the structure can alternatively be described as composed of layers. The volume between $z=+\frac{1}{4}$ and $z=-\frac{1}{4}$ in the unit cell constitutes the thickness of one layer and there are two layers per unit cell. A view of one layer down the positive c axis is given in Fig. 1.

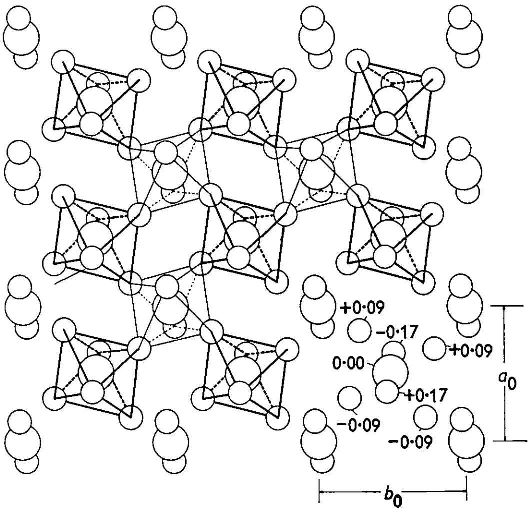

Fig. 1. The structure of one layer in $UO_2(OH)_2$ viewed down the positive c axis. Large circles are uranium atoms, small circles are oxygen atoms. Uranyl oxygen atoms are above and below the uranium atom and are nearly perpendicular to the layer. Hydroxyl oxygen atoms are at the remaining four vertices of the octahedron. Numbers represent the positional parameter z as a fraction of the unit cell edge.

The layers are composed of octahedra, each octahedron sharing four corners with other octahedra. Each octahedron has one uranium atom centrally located and six oxygen atoms at the vertices of the octahedron.

Table 2. *Observed and calculated structure factors for* $UO_2(OH)_2$

If $|F_o|$ is negative, the minus sign means less than. The terms A and B are as defined in Cromer, Larson & Roof (1964)

h	k	ℓ	$\|F_o\|$	$\|F_c\|$	A	B
0	2	0	176	225	220	50
0	4	0	159	181	175	43
0	6	0	102	98	91	34
0	8	0	65	58	53	25
2	0	0	221	206	199	51
2	1	0	37	40	-40	-0
2	2	0	218	221	215	49
2	3	0	-17	6	6	-1
2	4	0	143	140	133	42
2	5	0	18	13	-13	-1
2	6	0	107	96	90	34
2	7	0	-18	2	-1	-2
4	0	0	169	154	146	49
4	1	0	26	9	9	-1
4	2	0	157	149	141	46
4	3	0	-16	21	-21	-2
4	4	0	96	115	108	40
4	5	0	-13	4	-3	-3
4	6	0	72	84	77	32
6	0	0	128	131	123	45
6	1	0	-20	3	-3	-1
6	2	0	117	114	106	43
6	3	0	-18	3	1	-3
6	4	0	77	98	90	37
0	2	1	20	16	16	-1
0	4	1	-13	10	-10	-1
0	6	1	16	2	1	-1
0	8	1	-18	5	-5	-1
1	1	1	308	271	266	51
1	2	1	-18	7	7	-0
1	3	1	184	196	190	46
1	4	1	19	14	-14	-1
1	5	1	121	124	118	39
1	6	1	-15	4	4	-1
1	7	1	91	77	72	29
1	8	1	-18	5	-5	-1
2	1	1	38	31	31	-0
2	2	1	-22	3	-3	-1
2	3	1	-18	2	2	-0
2	4	1	-17	3	3	-1
2	5	1	-17	3	3	-0
2	6	1	-17	7	-7	-1
2	7	1	-18	3	-3	-0
3	1	1	221	187	181	49
3	2	1	-21	15	-15	-1
3	3	1	139	148	141	45
3	4	1	-15	3	-2	-2
3	5	1	110	115	109	37
3	6	1	-16	10	-9	-2
3	7	1	72	64	58	28
4	1	1	22	10	-10	-1
4	2	1	-22	7	-7	-1
4	3	1	-17	3	-3	-1
4	4	1	-15	8	-8	-1
4	5	1	-13	7	-6	-0
4	6	1	-14	3	-3	-1
5	1	1	155	139	131	46
5	2	1	-21	4	-3	-2
5	3	1	128	125	118	42
5	4	1	-15	7	-7	-3
5	5	1	75	83	76	35
6	1	1	-22	8	-7	-1
6	2	1	-22	5	-5	-1
6	3	1	-19	7	-7	-1
6	4	1	-16	4	-4	-1
7	1	1	103	102	93	42
7	2	1	-23	2	-1	-2
0	0	2	195	263	258	51
0	2	2	161	197	190	49
0	4	2	143	160	155	42
0	6	2	104	96	90	34
0	8	2	70	57	51	24
1	0	2	-22	11	-11	-0
1	1	2	-29	12	-12	-1
1	2	2	47	46	46	-0
1	3	2	-15	9	9	-2
1	4	2	-14	10	-10	-0
1	5	2	16	12	-11	-3
1	6	2	-16	2	2	-0
1	7	2	-17	5	-5	-3
2	0	2	239	218	213	50
2	1	2	-23	9	-9	-0
2	2	2	242	208	202	48
2	3	2	-18	5	5	-1
2	4	2	134	141	135	42
2	5	2	-16	7	-7	-1
2	6	2	102	93	87	33
2	7	2	-18	3	-2	-2
3	0	2	24	17	17	-1
3	1	2	22	18	18	-1
3	2	2	-21	4	-4	-1
3	3	2	23	21	-21	-2
3	4	2	-14	3	-3	-1
3	5	2	16	3	-1	-2
3	6	2	-16	1	1	-1
3	7	2	-17	8	-8	-3
4	0	2	194	174	168	48
4	1	2	-20	6	6	-1
4	2	2	168	157	150	46
4	3	2	-17	8	-8	-2
4	4	2	110	117	110	40
4	5	2	-14	5	-4	-3
4	6	2	77	79	73	32
5	0	2	-20	10	-10	-2
5	1	2	-20	14	-14	-1
5	2	2	-21	18	-18	-2
5	3	2	-17	6	-5	-2
5	4	2	-15	2	-2	-1
5	5	2	-14	8	-8	-2
6	0	2	117	119	110	44
6	1	2	-21	6	-6	-1
6	2	2	105	106	97	42
6	3	2	-19	8	-8	-3
6	4	2	78	87	79	37
7	0	2	-23	9	-9	-2
7	1	2	-23	1	-0	-0
0	2	3	18	8	8	-2
0	4	3	17	23	-23	-3
0	6	3	18	5	-3	-4
1	1	3	247	202	196	49
1	2	3	-17	0	-0	-0
1	3	3	149	168	162	45
1	4	3	-14	2	2	-1
1	5	3	113	119	113	37
1	6	3	-16	3	-3	-1
1	7	3	81	71	65	28
2	1	3	-21	2	-1	-1
2	2	3	-20	17	-16	-2
2	3	3	-17	10	-10	-1
2	4	3	-16	4	-2	-3
2	5	3	-16	3	3	-1
2	6	3	-17	16	-16	-4
2	7	3	-17	4	-4	-0
3	1	3	219	196	191	48
3	2	3	-20	7	7	-1
3	3	3	156	157	151	43
3	4	3	-14	3	-2	-2
3	5	3	105	103	96	36
3	6	3	-16	5	-5	-2
3	7	3	73	66	59	28
4	1	3	-20	9	-9	-2
4	2	3	-20	4	-4	-2
4	3	3	-16	2	0	-2
4	4	3	16	12	-12	-3
4	5	3	-14	10	-9	-1
4	6	3	-14	7	-6	-4
5	1	3	139	136	129	45
5	2	3	-20	5	-5	-2
5	3	3	112	110	103	41
5	4	3	-15	10	-9	-3
5	5	3	75	82	75	34
6	1	3	-21	6	-6	-3
6	2	3	-21	3	-3	-2
6	3	3	-19	9	-8	-2
6	4	3	-16	6	-6	-3
7	1	3	85	88	79	40
0	0	4	146	168	161	48
0	2	4	160	201	195	46
0	4	4	121	130	124	40
0	6	4	93	92	86	32
1	0	4	48	55	-55	-1
1	1	4	-22	20	-20	-1
1	2	4	-16	3	3	-1
1	3	4	-14	11	-10	-3
1	4	4	18	13	-13	-1
1	5	4	17	18	-18	-5
1	6	4	-15	2	2	-0
1	7	4	-17	11	-10	-5
2	0	4	212	207	201	47
2	1	4	-19	19	19	-0
2	2	4	179	166	159	45
2	3	4	-16	8	-8	-1
2	4	4	128	133	127	40
2	5	4	-16	2	1	-1
2	6	4	90	85	79	32
2	7	4	-17	5	-4	-1
3	0	4	-18	11	-11	-2
3	1	4	23	9	9	-1
3	2	4	-19	15	-15	-2
3	3	4	18	19	-19	-3
3	4	4	-14	4	-3	-2
3	5	4	-15	8	-6	-5
3	6	4	-16	2	-1	-1
4	0	4	159	158	151	45
4	1	4	-19	9	-9	-1
4	2	4	145	138	131	43
4	3	4	-16	3	2	-2
4	4	4	100	109	102	38
4	5	4	-14	8	-8	-2
4	6	4	70	69	62	30
5	0	4	-19	4	2	-3
5	1	4	-19	5	-5	-1
5	2	4	-19	4	-3	-3
5	3	4	-18	4	2	-3
5	4	4	-15	3	1	-2
5	5	4	-14	10	-9	-4
6	0	4	100	104	95	42
6	1	4	-20	2	-2	-1
6	2	4	89	100	92	40
6	3	4	-18	9	-9	-2
0	2	5	14	19	-18	-3
0	4	5	21	20	-19	-5
0	6	5	16	16	-15	-6
1	1	5	196	191	185	46
1	2	5	-15	10	-10	-0
1	3	5	140	147	141	42
1	4	5	15	8	8	-1
1	5	5	108	106	100	35
1	6	5	-15	8	-8	-1
1	7	5	74	63	57	27
2	1	5	22	26	-26	-2
2	2	5	-17	15	-14	-3
2	3	5	21	9	-9	-1
2	4	5	-16	15	-14	-5
2	5	5	-16	3	-3	-1
2	6	5	-16	17	-16	-6
2	7	5	-17	2	-1	-1
3	1	5	147	142	135	44
3	2	5	19	2	-1	-1
3	3	5	125	129	123	40
3	4	5	-14	11	-11	-1
3	5	5	82	85	79	34
3	6	5	-16	2	-1	-2
4	1	5	-18	6	-5	-3
4	2	5	-18	3	-0	-3
4	3	5	-16	4	-2	-3
4	4	5	-14	11	-10	-5
4	5	5	-14	4	-4	-2
4	6	5	-15	11	-9	-6
5	1	5	112	117	109	41
5	2	5	-18	5	-4	-1
5	3	5	92	94	86	38
5	4	5	-15	6	-5	-2
6	1	5	-20	6	-4	-4
6	2	5	-19	4	-3	-2
6	3	5	-18	7	-6	-4
0	0	6	150	172	166	44
0	2	6	169	186	181	42
0	4	6	113	108	102	37
0	6	6	91	81	75	30
1	0	6	-16	3	3	-1
1	1	6	-18	4	-4	-2
1	2	6	-15	8	-8	-1
1	3	6	16	19	-19	-5
1	4	6	-14	1	-0	-1
1	5	6	-15	18	-16	-7
1	6	6	-15	1	-1	-0
1	7	6	-17	16	-15	-7
2	0	6	160	164	158	43
2	1	6	19	8	8	-0
2	2	6	127	127	120	41
2	3	6	17	16	-16	-1
2	4	6	108	111	105	36
2	5	6	-15	2	2	-1
2	6	6	80	72	66	29
3	0	6	-17	11	-11	-3
3	1	6	-17	9	-9	-2
3	3	6	-15	9	-8	-4
3	4	6	-14	4	-3	-2
3	5	6	-15	16	-15	-6
3	6	6	-16	5	-5	-1
4	0	6	113	113	105	41
4	1	6	20	15	-15	-0
4	2	6	105	106	99	39
4	3	6	-16	2	1	-1
4	4	6	80	91	84	35
4	5	6	-14	9	-9	-2
5	0	6	-18	14	-13	-4
5	1	6	-18	2	-2	-1
5	2	6	-18	9	-8	-4
5	3	6	-17	10	-10	-4
5	4	6	-15	10	-9	-3
6	0	6	92	92	84	38
6	1	6	-19	4	4	-1
6	2	6	81	93	86	37
0	2	7	14	16	-15	-4
0	4	7	15	11	-10	-6
0	6	7	16	24	-23	-8
1	1	7	149	147	141	41
1	2	7	17	7	-7	-0
1	3	7	118	118	112	37
1	4	7	-14	1	1	-0
1	5	7	94	86	80	32
1	6	7	-16	4	-4	-0
2	1	7	-17	6	6	-2
2	2	7	-16	5	-3	-4
2	3	7	-16	4	4	-2
2	4	7	-15	22	-21	-6
2	5	7	-15	7	-6	-1
2	6	7	-16	15	-13	-7
3	1	7	109	116	109	39
3	2	7	-16	4	-4	-1
3	3	7	97	102	96	36
3	4	7	15	7	-7	-1
3	5	7	70	75	68	31
4	1	7	-17	13	-12	-4
4	2	7	-17	14	-13	-3
4	3	7	-15	16	-16	-3
4	4	7	-14	16	-15	-6
4	5	7	-14	3	-2	-3
5	1	7	91	95	87	37
5	2	7	-17	2	-2	-1
5	3	7	75	82	75	34
6	1	7	-19	18	-17	-5
0	0	8	117	118	111	38
0	2	8	122	113	106	37
0	4	8	93	89	82	33
0	6	8	72	65	59	27
1	0	8	25	25	25	-1
1	1	8	-16	5	4	-2
1	2	8	-14	8	-8	-1
1	3	8	15	18	-17	-6
1	4	8	17	6	6	-1
1	5	8	-15	17	-15	-8
1	6	8	-16	3	-3	-1
2	0	8	119	122	116	38
2	1	8	-16	1	-1	-0
2	2	8	104	109	102	36
2	3	8	-15	2	-2	-0
2	4	8	89	89	83	32
2	5	8	-15	1	-1	-1
3	0	8	-16	7	-6	-3
3	1	8	18	17	-17	-2
3	2	8	-15	5	-4	-3
3	3	8	-15	9	-7	-5
3	4	8	-14	7	-7	-2
3	5	8	-15	22	-21	-7
4	0	8	96	101	94	36
4	1	8	-17	0	-0	-0
4	2	8	89	96	90	35
4	3	8	-15	2	2	-1
4	4	8	70	74	67	31
5	0	8	-18	22	-21	-5
5	1	8	-18	3	-2	-2
5	2	8	-17	14	-13	-5
5	3	8	-16	18	-18	-5
0	2	9	14	12	-11	-4
0	4	9	16	14	-12	-7
1	1	9	100	96	90	35
1	2	9	-14	5	5	-0
1	3	9	90	89	83	32
1	4	9	-14	4	-4	-0
1	5	9	72	66	60	28
2	1	9	18	7	-6	-2
2	2	9	-15	9	-8	-4
2	3	9	-16	5	-5	-2
2	4	9	-15	22	-21	-7
2	5	9	-16	6	-6	-2
3	1	9	98	103	98	34
3	2	9	-15	3	3	-0
3	3	9	85	82	76	31
3	4	9	-15	2	2	-1
4	1	9	-17	10	-9	-4
4	2	9	-16	13	-12	-4
4	3	9	-15	12	-12	-4
5	1	9	71	76	69	32
0	0	10	94	95	89	32
0	2	10	82	74	68	31
0	4	10	76	73	68	28
1	0	10	-15	7	-7	-1
1	1	10	-17	6	-5	-2
1	2	10	16	13	-13	-1
1	3	10	-14	18	-17	-6
1	4	10	-15	1	-0	-1
2	0	10	91	82	76	32
2	1	10	-16	4	-4	-0
2	2	10	84	87	81	31
2	3	10	16	8	8	-0
2	4	10	74	65	59	27
3	0	10	17	15	-15	-3
3	1	10	-16	9	-8	-2
3	2	10	-15	9	-8	-3
3	3	10	-15	11	-9	-6
4	0	10	82	77	71	31
4	1	10	-17	6	6	-0
4	2	10	72	73	66	30
0	2	11	-14	13	-12	-4
0	4	11	-15	20	-19	-7
1	1	11	78	78	72	29
1	2	11	-15	4	4	-0
1	3	11	77	68	63	27
1	4	11	-15	4	-4	-0
2	1	11	-16	14	-13	-2
2	2	11	-15	12	-11	-4
2	3	11	-15	9	-9	-2
3	1	11	72	65	59	28
3	2	11	-15	3	-3	-0
0	0	12	89	81	76	26
0	2	12	65	61	56	25
1	0	12	-16	8	-8	-1
1	1	12	-17	9	-9	-2
1	2	12	-15	2	1	-1
2	0	12	64	56	50	26
2	1	12	-16	6	-6	-0

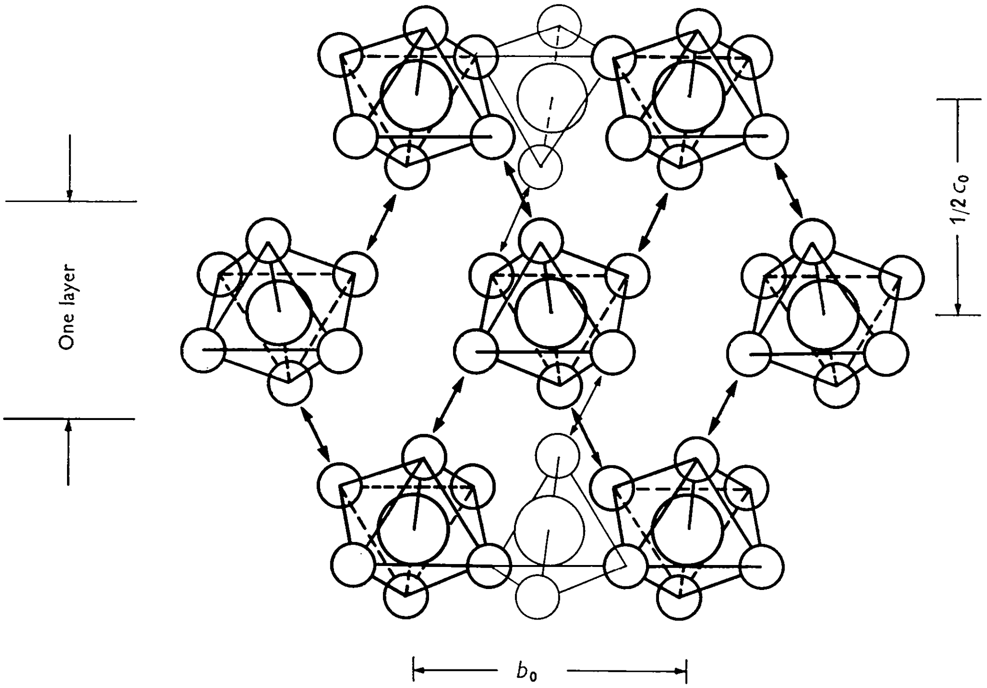

Fig. 2. The structure of $UO_2(OH)_2$ viewed down the positive *a* axis. The central atoms of the heavy lined octahedra are located at $x = \frac{1}{2}$. The central atoms of the light lined partial octahedra are located at $x = 0$ at the top of the drawing and at $x = 1$ at the bottom of the drawing. Proposed hydrogen bond contacts of 2·69 Å are indicated by ↔.

Table 3. *Interatomic distances in* $UO_2(OH)_2$

U–2 O(1)	1·823 ± 0·048 Å
–2 O(2)	2·237 ± 0·059
–2 O(2)	2·434 ± 0·057
O(1)–2 O(1)	3·282 ± 0·050
–2 O(1)	3·391 ± 0·038
–O(2)	2·692 ± 0·083
–O(2)	2·767 ± 0·099
–O(2)	2·899 ± 0·099
–O(2)	3·260 ± 0·102
–O(2)	3·383 ± 0·071
–O(2)	4·355 ± 0·089
–U	1·823 ± 0·048
O(2)–O(1)	2·692 ± 0·083
–O(1)	2·766 ± 0·099
–O(1)	2·899 ± 0·099
–O(1)	3·260 ± 0·102
–O(1)	3·383 ± 0·076
–O(1)	4·355 ± 0·089
–2 O(2)	3·227 ± 0·024
–O(2)	3·927 ± 0·084
–U	2·236 ± 0·059
–U	2·434 ± 0·057

The uranyl oxygen atoms are roughly perpendicular to the layer, the hydroxyl oxygen atoms are at the remaining four vertices of the octahedron and are shared with other octahedra. The layers are hydrogen-bonded together, the hydrogen bond extending from a hydroxyl oxygen atom in one layer to the uranyl oxygen atom in the adjacent layer. The layer structure offers an explanation for the easy cleavage, perpendicular to the *c* axis, observed on the single crystals.

Fig. 2 is a view down the positive *a* axis of the $UO_2(OH)_2$ structure. The proposed hydrogen bond contacts of 2·69 Å are indicated by ↔. The observed hydrogen bond distance of 2·69 ± 0·08 Å is in good agreement with the value 2·72 ± 0·04 Å given by Wallwork (1962) for the hydrogen bond type Y–H ··· Z where Y–H is the donor group OH and Z is the acceptor group O. Fig. 3 illustrates in greater detail an isolated octahedron viewed down the positive *a* axis. Interatomic distances are in Å.

The interrelated agreement of the U–O bond lengths

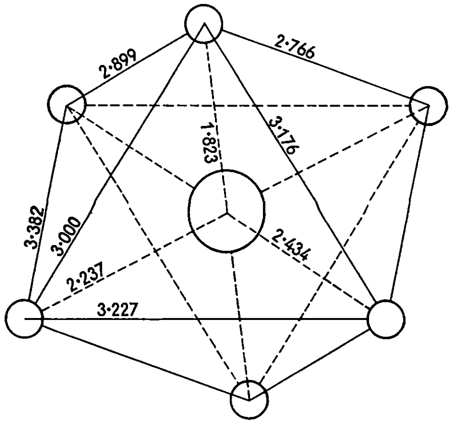

Fig. 3. Interatomic distances in Å in an isolated octahedron of $UO_2(OH)_2$ viewed down the positive *a* axis. Distances were calculated from atomic positions given in Table 2.

in the octahedra can be determined by reference to a diagram of uranyl bond length *vs.* fractional valence given by Zachariasen (1954). The line relating these two quantities appears to have a slight curvature, and thus the equation of this line might reasonably be a quadratic. In a least-squares fit of a quadratic to the data, the coefficient of the X^2 term of the quadratic is small and does not deviate significantly from zero. This indicates that a straight line may fit the data as well as or better than a quadratic. In fact, a lower variance is obtained with a least-squares fit of a straight line to the data than with a quadratic and, therefore, the linear function is to be preferred for the representation of the data.

From the coefficients of the linear fit it is possible, by straightforward statistical techniques, to relate a bond length with a standard deviation to a fractional valence with a standard deviation. In Table 4 are given the interatomic distances and the associated fractional valences.

Table 4. *Interatomic distances and associated fractional valences in* $UO_2(OH)_2$

Atoms	Interatomic distances	Fractional valences
U–2 O(1)	1·82 ± 0·05 Å	1·50 ± 0·18
–2 O(2)	2·24 ± 0·06	0·71 ± 0·16
–2 O(2)	2·43 ± 0·06	0·35 ± 0·14

The sum of the fractional valences for the six bonds is 5·12 ± 0·39. The question now arises as whether the number 5·12 is significantly different from the normal valence of 6·00. By utilizing the statistical t test at the 95% confidence level, $t = 2·45$ for a population of 6. Then, $2·45 \times 0·39 = 0·96$, and $5·12 + 0·96 = 6·08$. Thus at the 95% confidence level there is no significant difference between the empirically derived valence and the normal valence.

It has come to our attention that Zachariasen (1963) has devised an improved expression for the effects of secondary extinction. The ratio Zachariasen's formula/Dawson's formula is 1·00 for $2\theta = 0°$, 1·02 for $2\theta = 30°$ and 1·11 for $2\theta = 45°$. For Mo $K\alpha$ intensity data, where strong reflections occur only at low values of 2θ, it can be seen that no significant difference should occur in the structural parameters regardless of which formula is used. Zachariasen's formula applied to the data of the present paper resulted in no effective change in the parameters. This indicated that it would not be worthwhile to re-examine the Mo data of UF_4 and $UMoC_2$ in the light of Zachariasen's new formula.

References

Aronson, S. (1958). Bettis Technical Review, WAPD-BT-10, p. 93.

Belle, J. (1961). *Uranium dioxide: Properties and nuclear applications.* p. 398. Available from Superintendent of Documents, U.S. Government Printing Office, Washington 25, D. C., U.S.A.

Burnham, W. C. (1962). I.U.Cr. *World List of Crystallographic Computer Programs.* Program 338.

Cromer, D. T., Larson, A. C. & Roof, Jr., R. B. (1964). *Acta Cryst.* **17**, 272.

Dawson, J. K., Wait, E., Alcock, K. & Chilton, D. R. (1956). *J. Chem. Soc.* 3531.

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.

Larson, A. C., Roof, Jr., R. B. & Cromer, D. T. (1964). *Acta Cryst.* **17**, 555.

Roof, R. B. (1961). *Acta Cryst.* **14**, 934.

Wallwork, S. C. (1962). *Acta Cryst.* **15**, 758.

Zachariasen, W. H. (1954). *Acta Cryst.* **7**, 795.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1964). **17**, 705

The Crystal Structure and Molecular Configuration of Trisacetylacetonatomanganese(III)*

By B. Morosin and J. R. Brathovde

Sandia Corporation, Albuquerque, New Mexico, U.S.A.

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The crystal structure and molecular configuration of trisacetylacetonatomanganese(III) has been determined by X-ray diffraction techniques. The structure consists of discrete molecules linked together by van der Waals forces. The distortion of the octahedral configuration of oxygen ligands about the manganese atom appears to be the result of altered oxygen–metal–oxygen bond angles rather than of a Jahn–Teller mechanism.

Introduction

The departure from regular octahedral configuration for the case of nine 3*d* electrons, *i.e.* copper(II) compounds, is well documented (Griffith & Orgel, 1957). However, probably because of chemical instability, only a few examples of structure determinations for the transition elements with four unpaired electrons are available. These consist of simple halide compounds of Cr^{II} (Tracy, Gregory, Lingafelter, Dunitz,

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