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THE CRYSTAL STRUCTURE OF URANYL NITRATE HEXAHYDRATE

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Introduction

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, readily forms rhombic bipyramidal crystals whose axial ratios are given[1] as 0.8737:1:0.6088. The reflections from three faces of this crystal of the X-radiation from a tube with a tungsten anticathode have been investigated by Clark[2] using an ionization spectrometer. From the face (010) he obtained superposed on the general radiation a number of peaks which he interpreted as being due to the characteristic L-radiation of uranium excited in the crystal and reflected by it. For instance, when the incident beam made the angle 1°32′ with the crystal face he found a peak which he takes as $L\gamma_1$ (wave length 0.61283 Å.). Substituting these values in the equation $n\lambda = 2d\sin\theta$, one obtains $d_{010}/n = 11.45$ Å. This distance, 11.45 Å., Clark takes as the length of one of the edges of the unit parallelopiped. He obtained in a similar manner 7.93 and 13.01 Å. for the other two edges. He states that "the unit parallelopiped contains four molecules, as calculated from the density, 2.807. The uranium atoms are, therefore, at the corners and at the center of the faces....."

The conclusion that the structure is face-centered simply because there are four molecules in the unit is, however, unjustified; for the theory of space groups shows that numerous other arrangements with this number of molecules in the unit and with the requisite symmetry are possible. Moreover, this conclusion is not in agreement with Clark's assignment of wave lengths to his peaks. For, if the structure is face-centered, only odd orders of reflection can appear from the pinacoids; and if $d_{010} = 11.45$ Å., the smallest angle of reflection that can occur with a given wave length from (010) will be obtained from $n\lambda = 2d\sin\theta$ by placing $d = 11.45$ and $n = 2$; and for $\lambda = 0.61283$ Å. this smallest angle is 3°4′, not 1°32′.

Two possible reasons for this discrepancy suggest themselves: (1) the origin of the peaks may be other than that supposed by Clark, or (2) the structure may not be that given by him. Our own results, described below, indicate that both of these reasons are valid.

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[1] Groth, "Chemische Kristallographie," Engelmann, Leipzig, **2**, 142 (1908).

[2] Clark, THIS JOURNAL, **46**, 379 (1924).

The Experimental Method

Crystals of the pure salt, $UO_2(NO_3)_2.6H_2O$, were dissolved in a small amount of water, and the solution was allowed to evaporate over sulfuric acid in a desiccator. For the identification of the faces on the resulting crystals interfacial angles were measured on a reflection goniometer, and the extinction directions observed in a polarizing microscope. The forms observed were those previously reported;[1] our crystals were, however, usually tabular on *a* $\{100\}_G$, rather than on *b* $\{010\}_G$. The subscript G is here placed on all indices which are based on the crystallographic axes given by Groth.[1]

Using the method of reflection from the face of a rotating crystal, spectral photographs of the radiation from a molybdenum target X-ray tube were obtained from the three pinacoids; (since $\{001\}_G$ was not developed on the crystals, the crystal was ground with fine carborundum in a plane normal to $\{100\}_G$ and $\{010\}_G$). The tube was operated at a peak voltage of 60 kv. At least two spectral photographs were made from each pinacoid with the crystal in different orientations.

Using a tungsten target tube operated at a peak voltage of 52 kv, Laue photographs were taken with the incident beam making small angles with the normals to $(100)_G$ and $(010)_G$. The indices corresponding to the spots occurring on these photographs were obtained from gnomonic projections.[3]

The density of the salt was determined by finding with a pycnometer the density of a liquid in which a small crystal remained suspended. Two such determinations gave for the density 2.744 and 2.740 g. per cc.

The Unit of Structure

The spectral data given in Table I lead to the following values of d/n: $(100)_G$, 5.71; $(010)_G$, 6.575; $(001)_G$, 2.005 Å. Examination of the indices and angles of reflection of a number of Laue spots showed that the smallest values which can be assigned to n to give an integral number of molecules in the unit and not to require that the Laue spots be produced by wave lengths below those known to be present in the general radiation are: $(100)_G$, $n = 2$; $(010)_G$, $n = 2$; $(001)_G$, $n = 4$. The smallest possible unit of structure accordingly has these values[4] of d: $(100)_G$, 11.42; $(010)_G$, 13.15; $(001)_G$, 8.02 Å., and contains 4 molecules. From the density, 2.742, the calculated number of $UO_2(NO_3)_2.6H_2O$ per unit is 3.99.

[3] Wyckoff, *Am. J. Sci.*, **50**, 322 (1920).

[4] It will be observed that Clark's values can be brought into approximate agreement with ours by making a suitable permutation of indices. Whether this permutation is permissible is not clear. However, the facts described subsequently in this paper make this approximate agreement appear fortuitous.

TABLE I

SPECTRAL DATA FROM $UO_2(NO_3)_2.6H_2O$

$(hkl)_G$	Line	Observed angle of reflection	$\frac{d}{n}$	Relative intensities[a]
$(100)_G$	Mo$K\beta$	3° 10.4′	$^1/_2 \times 11.40$	m
	α	3 33.5	$^1/_2 \times 11.44$	s
	β	6 21.2	$^1/_4 \times 11.40$	vw
	α	7 7.6	$^1/_4 \times 11.43$	m
	β	9 33.0	$^1/_6 \times 11.42$	mw
	α_1	10 43.0	$^1/_6 \times 11.42$	ms
	α_2	10 45.2	$^1/_6 \times 11.44$	m
	β	12 45.7	$^1/_8 \times 11.42$	vw
	α_1	14 19.7	$^1/_8 \times 11.43$	mw
	α_1	18 2.7	$^1/_{10} \times 11.42$	w
$(010)_G$	β	2 44.5	$^1/_2 \times 13.17$	mw
	α	3 5.8	$^1/_2 \times 13.15$	s
	β	5 31.4	$^1/_4 \times 13.12$	m
	α	6 10.7	$^1/_4 \times 13.19$	vs
	β	8 16.8	$^1/_6 \times 13.15$	mw
	α	9 18.5	$^1/_6 \times 13.16$	ms
	β	11 4.3	$^1/_8 \times 13.14$	w
	α	12 27.7	$^1/_8 \times 13.16$	m
	β	13 53.5	$^1/_{10} \times 13.14$	w
	α_1	15 37.0	$^1/_{10} \times 13.16$	m
	α_1	15 43.4	$^1/_{10} \times 13.15$	mw
	β	16 47.0	$^1/_{12} \times 13.12$	vw
	α_1	18 53.3	$^1/_{12} \times 13.12$	w
$(001)_G$[b]	γ	8 53.6	$^1/_4 \times 8.02$	vw
	β	9 4.0	$^1/_4 \times 8.01$	m
	α_1	10 11.0	$^1/_4 \times 8.01$	s
	α_2	10 13.2	$^1/_4 \times 8.02$	ms

[a] The abbreviations are: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak.

[b] On several spectral photographs from $(001)_G$ taken with the crystal in different orientations, reflections were observed in the plane of the $(001)_G$ reflections which could not be accounted for as ordinary reflections from $(001)_G$; for example, a line of medium intensity at $\vartheta = 5°22.2'$ and a weak line at $4°47'$. These reflections have been shown to be similar in their origin to the diffuse spots near the central image observed on some Laue photographs [Dickinson, *Phys. Rev.*, **22**, 199 (1923)]; these phenomena and their explanation will be the subject of a later paper.

The Space Lattice

The space lattice underlying the entire atomic arrangement can be determined by a consideration of the character of the indices of the planes giving first order reflections; for no first order reflections can occur in the following cases:

Lattice Γ_3''', face-centered; h, k, or l even.
Lattice Γ_0'', body-centered; $h + k + l$ odd.
Lattice Γ_0', end-centered on (001); $h + k$ odd.

Lattice Γ_0', end-centered on (010); $h + l$ odd.
Lattice Γ_0', end-centered on (100); $k + l$ odd.

In Table II are given representative data from one Laue photograph. Reference to these data shows that planes of each of these types except the last (those having $k + l$ odd) gave first order reflections. This fact definitely eliminates the face-centered and body-centered lattices. If the lattice were the simple one, Γ_0, no such general types of planes would fail to give first-order reflections, and this lattice would not account for the observed absence in the first order of planes having $k + l$ odd, many of which were in positions favorable to reflection. These absences are, however, accounted for by the lattice Γ_0' end-centered on $(100)_G$.

TABLE II

LAUE DATA FROM $UO_2(NO_3)_2.6H_2O$; PHOTOGRAPH NO. 8, THROUGH $(100)_G$

$(hkl)_G$	(hkl)	$n\lambda$ Å.	d Å.	Estimated intensity[a]	S for $u = 0.13$
104	041	0.44	1.97	0.05	1.25
$1\bar{1}4$	$\bar{1}41$	.43	1.94	a	0
$1\bar{6}2$	$\bar{6}21$	.45	1.89	8	9.98
124	241	.42	1.88	0.25	1.25
$1\bar{2}4$	$\bar{2}41$	.38	1.88	.25	1.25
$1\bar{5}3$	$\bar{5}31$	.38	1.84	3.5	6.37
$1\bar{7}1$	$\bar{7}11$	.45	1.79	2.5	7.29
144	441	.35	1.69	0.05	1.25
163	631	.40	1.67	a	0
$1\bar{8}0$	$\bar{8}01$	.39	1.62	a	0
182	821	.37	1.51	3.5	9.98
$1\bar{8}2$	$\bar{8}21$	.41	1.51	3.5	9.98
191	911	.37	1.42	1.3	7.29
$19\bar{1}$	$9\bar{1}1$	.44	1.42	1.2	7.29
$1\bar{8}3$	$\bar{8}31$	.37	1.39	a	0
$1\bar{5}5$	$\bar{5}51$	.43	1.35	1.4	8.09
1.10.0	10.0.1	.35	1.30	a	0
$1\bar{2}6$	$\bar{2}61$	.44	1.29	1.5	9.82
$1.10.\bar{1}$	$10.\bar{1}.1$	.36	1.29	a	0
$1\bar{6}5$	$\bar{6}51$	.39	1.28	a	0
$19\bar{3}$	$9\bar{3}1$	.39	1.27	0.8	6.37
$1\bar{3}6$	$\bar{3}61$	.41	1.27	a	0
$18\bar{4}$	$8\bar{4}1$	.40	1.26	a	1.25
$2\bar{6}5$	$\bar{6}52$	.40	1.26	a	0
$1.10.\bar{2}$	$10.\bar{2}.1$	.36	1.24	1.8	9.98
$1\bar{4}6$	$\bar{4}61$	.38	1.23	1.8	9.82
$14\bar{6}$	$4\bar{6}1$	.42	1.23	1.8	9.82
$17\bar{5}$	$7\bar{5}1$	.39	1.21	0.9	8.09
275	752	.41	1.19	.6	5.88
$2\bar{7}5$	$\bar{7}52$	.35	1.19	.7	5.88
$1\bar{5}6$	$5\bar{6}1$	.39	1.18	a	0
$19\bar{4}$	$9\bar{4}1$	.36	1.17	a	0
$1.10.\bar{3}$	$10.\bar{3}.1$	.34	1.17	a	0

TABLE II (*Concluded*)

$(hkl)_G$	(hkl)	$n\lambda$ Å.	d Å.	Estimated intensity[a]	S for $u = 0.13$
$18\bar{5}$	$8\bar{5}1$	.35	1.14	a	0
$16\bar{6}$	$6\bar{6}1$	.36	1.13	1.6	9.82
$11\bar{7}$	$1\bar{7}1$	.36	1.13	0.35	5.36
285	852	.37	1.12	a	0
$2.\bar{11}.2$	$\bar{11}.2.2$	.36	1.12	a	0
$13\bar{7}$	$3\bar{7}1$	.35	1.10	0.2	5.36
$2.\bar{11}.\bar{3}$	$\bar{11}.\bar{3}.2$	.42	1.07	.6	7.71
$29\bar{5}$	$\bar{9}52$	.45	1.06	.25	5.88
$3\bar{5}7$	$\bar{5}73$	.41	1.01	.25	5.36
$2.13.\bar{1}$	$13.\bar{1}.2$	.39	0.99	.2	6.85
367	673	.41	.98	a	0
$2.13.\bar{2}$	$13.\bar{2}.2$	.39	.97	a	0
377	773	.38	.94	0.15	5.36
$2.\bar{11}.\bar{5}$	$\bar{11}.\bar{5}.2$	.35	.94	.15	5.88
$2.13.\bar{3}$	$13.\bar{3}.2$	.37	.93	.15	7.71
$3.\bar{12}.4$	$\bar{12}.4.3$	.37	.93	a	1.25
3.14.0	14.0.3	.46	.91	a	0
3.10.6	10.6.3	.38	.91	0.35	9.82
$3.\bar{14}.\bar{2}$	$\bar{14}.\bar{2}.3$	.40	.89	.2	9.98

[a] a signifies absent.

Discussion of Previous Conclusions

The complete absence of all odd orders of reflection from the pinacoids (Table I) makes it difficult to interpret any of Clark's[2] peaks as first-order reflections from these faces. Moreover, as shown above, the Laue photographic data definitely show that the underlying lattice is the end-centered one; and this again necessitates the absence of odd orders of reflection from two pinacoids. This makes it clear that at least some of the peaks observed by Clark did not arise from the excitation of the L-radiation of uranium within the crystal and its reflection by the pinacoids; for, as shown in the introduction, this explanation would necessitate interpreting some of the peaks as first-order reflections. The belief that[5] "the unit parallelopiped.....is face-centered" is, moreover, not substantiated by the work described in this paper. It is evident that for purposes of crystal structure analysis further investigation of the phenomenon reported by Clark and Duane[6] is desirable.

The Space Group

The holohedral space groups derived from the lattice Γ_0' are[7] V_h^{17}, V_h^{18}, V_h^{19}, V_h^{20}, V_h^{21}, V_h^{22}. Some of these may be definitely excluded

[5] Ref. 2, p. 384.

[6] Clark and Duane, *J. Opt. Soc.*, **7**, 455 (1923).

[7] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Inst. Pub., No. **318** (1922).

by a consideration of reflections from *prism* planes.[8] Prism planes having $h + k + l$ even cannot reflect in the first order if the space group is V_h^{18}, V_h^{21}, or V_h^{22}; those having $h + k + l$ odd cannot reflect in the first order if the space group is V_h^{20} or V_h^{22}. The presence of reflections of both of these types, as shown in Table III, definitely eliminates all of these space groups. Of the remaining two space groups V_h^{17} and V_h^{19} the former permits first-order reflections from planes of only two prism zones, while the latter permits such reflections from all three. No first-order reflections from planes of the type $(hk0)_G$ were observed on any photograph, although a number of such planes were in positions favorable to reflection. The evidence is thus in favor[9] of V_h^{17} as opposed to V_h^{19}.

For convenience in applying the theory of space groups, and in comparing structures with each other, it is desirable to assign the axes in agreement with the conventions adopted during the development of the theory of space groups. The coördinates of equivalent positions for V_h^{17} as tabulated[7] require that no first-order reflections take place from planes with $h + k$ odd or with $k = 0$. If the axes of $UO_2(NO_3)_2.6H_2O$ be chosen such that $d_{100} = 13.15$, $d_{010} = 8.02$, and $d_{001} = 11.42$ Å., the structure will be in agreement with this tabulation. The transformation from indices $(hkl)_G$ to those (hkl) conforming with space group usage is $h_G = l$, $k_G = h$, and $l_G = k$.

TABLE III

LAUE DATA FROM $UO_2(NO_3)_2.6H_2O$. PHOTOGRAPH NO. 6, THROUGH $(010)_G$

$(hkl)_G$	(hkl)	$n\lambda$ Å.	d Å.	Estimated intensity
$\bar{3}02$	$02\bar{3}$	0.40	2.76	8
$\bar{7}20$	$20\bar{7}$	.41	1.58	a
$0\bar{1}5$	$\bar{1}50$	.31	1.58	0.8
$03\bar{5}$	$3\bar{5}0$	.40	1.50	.6
$\bar{8}30$	$30\bar{8}$	.54	1.36	a
$0\bar{1}6$	$\bar{1}60$	.30	1.32	a
902	029	.40	1.21	1.2
$\bar{5}06$	$06\bar{5}$	.30	1.15	0.6
$0\bar{1}7$	$\bar{1}70$	.30	1.13	.3
$05\bar{7}$	$5\bar{7}0$	.40	1.04	.3
11.2.0	2.0.11	.54	1.03	a
11.0.2	0.2.11	.32	1.01	0.4
$\bar{1}\bar{1}.4.0$	$4.0.\bar{1}\bar{1}$	.37	0.98	a
13.2.0	2.0.13	.41	.87	a
$\bar{1}\bar{3}.6.0$	$6.0.\bar{1}\bar{3}$	.43	.82	a
$\bar{7}30$	$30\bar{7}$	2×0.37	2×0.76	0.15

[8] Niggli, "Geometrische Kristallographie des Discontinuums," Borntraeger, Leipzig, 1919, p. 497.

[9] The absence of all odd orders of reflection from the three pinacoids is further evidence in favor of V_h^{17}; for V_h^{19} can give odd orders of reflection from one pinacoid while V_h^{17} can give odd orders from none.

The Arrangement of the Uranium Atoms

In view of the large number of parameters involved, it seems at present impracticable to attempt a determination of the positions of all of the atoms in the unit of structure. However, information can be obtained concerning the positions of the uranium atoms. Uranium has the atomic number 92; the sum of the atomic numbers of the other atoms in $UO_2(NO_3)_2.6H_2O$ is 138 and the highest of these is 8. Consequently, especially in the case of planes having complicated indices and small interplanar distances, the intensity of reflection may be expected to be governed largely by the positions of the uranium atoms. We have, indeed, found it possible to assign positions to the uranium atoms which give a very consistent agreement between the general character of the observed intensities and the structure factors S calculated, neglecting all atoms but those of uranium.

There are the three following ways of arranging the four uranium atoms in a unit with the space-group symmetry V_h^{17}: (*a*) 000, $00\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; (*b*) $\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$; (*c*) $0u\frac{1}{4}$, $0\bar{u}\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}+u\ \frac{1}{4}$, $\frac{1}{2}\frac{1}{2}-u\ \frac{3}{4}$. If the uranium atoms alone are considered, and these without reference to their own symmetry, then (*a*) differs from (*b*) only by a translation of the whole structure along the H-axis, and (*c*) with $u = 0$ differs from (*a*) or (*b*) only by a translation of the whole structure; hence, in the present case, (*a*) and (*b*) are included in (*c*) and only the last need be considered. For first-order reflections (*c*) gives: $A = 4\bar{U}\cos 2\pi(uk + l/4)$; $B = 0$. In Fig. 1 are curves giving values of $S = \sqrt{A^2 + B^2}$ for a number of planes plotted against u from $u = 0$ to $u = 0.25$; this interval includes all distinct arrangements of the uranium atoms. The planes are divided into two classes: (1) those with l odd, and (2) those with l even. All planes of a given class with the same value of k have the same structure factor.

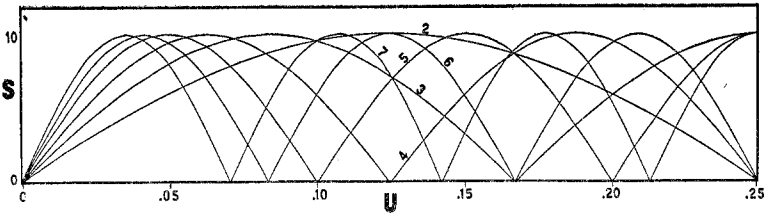

Fig. 1.—Values of S calculated for Arrangement *c*, with $4\bar{U} = 10$. The curves are for planes of Class 1, the number on the curve being the value of k. The curves also give values of S for planes of Class 2 with these values of k if u is made 0.25 at the left and 0 at the right of the figure.

Reference to the data of Table II shows that planes of Class 1 having $k = 4$ were found to reflect very weakly; those of Class 1 having $k = 2$ or

$k = 6$ reflected comparatively strongly. The structure factor due to the uranium atoms (Fig. 1) is in agreement with these facts only in the neighborhood of $u = 0.125$. A consideration of the reflections from other planes indicates for u a value near 0.13. Values of this structure factor for all planes of Table III are given in the 6th column. By comparing these values with the observed intensities it will be seen that this arrangement of the uranium atoms alone with $u = 0.13$ accounts satisfactorily for most of the abnormalities in intensity relations, and for all of the pronounced ones. If this value of u is altered by as much as 0.01 the agreement is in many cases destroyed.

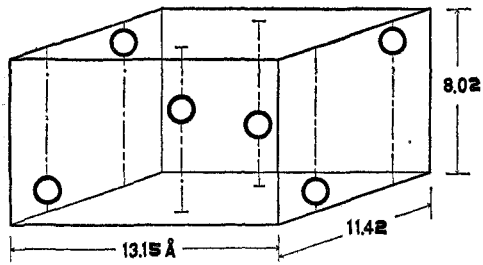

Fig. 2.—The arrangement of the uranium atoms in the unit of structure of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$.

This arrangement of the uranium atoms in the unit of structure is shown in Fig. 2.

Summary

Crystals of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, have been investigated, using both spectral photographs of the molybdenum K-radiation and Laue photographs, and the data have been interpreted with the aid of the theory of space groups. The unit of structure, which contains four $UO_2(NO_3)_2.6H_2O$, has $d_{100} = 13.15$, $d_{010} = 8.02$, and $d_{001} = 11.42$ Å., and is end centered on (001). The data indicate that the space-group symmetry is V_h^{17}, and that the uranium atoms are at $(0u\frac{1}{4})$ $(0\bar{u}\frac{3}{4})$ $(\frac{1}{2}\frac{1}{2} + u\ \frac{1}{4})$ $(\frac{1}{2}\frac{1}{2} - u\ \frac{3}{4})$ with $u = 0.13$. Referred to the axes used by Groth,[1] the above-mentioned interplanar distances are for the planes $(010)_G$, $(001)_G$, and $(100)_G$, respectively.

These results make unjustifiable Clark's interpretation[2] of his observed peaks as due to a characteristic radiation of the uranium atoms reflected by the pinacoids.

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