

## Uranyl(VI) Compounds. II. The Crystal Structure of Potassium Uranyl Sulfate Dihydrate, $K_2UO_2(SO_4)_2 \cdot 2H_2O$

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$K_2UO_2(SO_4)_2 \cdot 2H_2O$  crystallizes in the orthorhombic system, space group  $Pnma$ , with  $a = 13.806(4)$ ,  $b = 11.577(1)$ ,  $c = 7.292(1)$  Å and four formula weights in the unit cell. The structure was refined to  $R = 0.062$  for 1351 reflections. The uranyl ion is surrounded by five oxygen atoms, four of them belonging to sulfate groups and one to a water molecule. The mean bond lengths are: U–O(uranyl) 1.76, U–O(sulfate) = 2.36, and U–O(water) = 2.52 Å. Sulfate groups join the  $UO_7$  pentagonal bipyramids into layers which are tied together by potassium ions and noncoordinated water molecules.

$K_2UO_2(SO_4)_2 \cdot 2H_2O$  is one of the oldest known uranyl compounds.<sup>1</sup> Several studies have been carried out on its properties but the crystal structure has remained unknown although the unit cell dimensions and the space group have been published.<sup>2</sup> These data indicate that the potassium compound is isostructural with  $Rb_2UO_2(SO_4)_2 \cdot 2H_2O$ ,<sup>3</sup> while the corresponding ammonium compound has a different structure as shown by the recent structure determination carried out in this laboratory.<sup>4</sup> In order to be able to compare these two structure types, an X-ray analysis of  $K_2UO_2(SO_4)_2 \cdot 2H_2O$  was initiated.

### EXPERIMENTAL

$K_2UO_2(SO_4)_2 \cdot 2H_2O$  was crystallized at room temperature from an aqueous solution containing potassium and uranyl sulfates in equimolar amounts.<sup>5</sup> A plate-like crystal with approximate dimensions of  $0.3 \times 0.2 \times 0.1$  mm was selected for the X-ray diffraction measurement.

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The intensity data were collected with a Syntex P2<sub>1</sub> automatic diffractometer using graphite monochromatized MoK $\alpha$ -radiation. Accurate unit cell dimensions were obtained by means of a least-squares refinement applied to 25 centered reflections, all with  $2\theta > 40^\circ$ . The crystal data are summarized in Table 1. The  $\theta - 2\theta$  scan mode was used for the intensity data collection with a variable scan speed from 1 to  $3^\circ \text{ min}^{-1}$ . Of the 1941 independent reflections in the range  $5^\circ < 2\theta < 60^\circ$ , 1351 satisfied the criterion  $I > 3\sigma(I)$  and were used in the subsequent calculations. The intensities were corrected for Lorentz and polarization effects and for absorption from the  $\phi$ -scan data.

A three-dimensional Patterson map revealed the position of the uranium atom and its coordinates were refined. The remaining nonhydrogen atoms were found in the subsequent difference synthesis. A block-diagonal least-squares refinement with anisotropic temperature factors for uranium, potassium and sulfur led to the final value of 0.062 for the conventional  $R$ -index; the weighted  $R$ -index was 0.079 [ $w = 1/\sigma^2(F_0^2)$ ]. Scattering factors for neutral atoms were used in the refinement and, for uranium, a correction for the anomalous dispersion was applied.<sup>6</sup> The difference Fourier map calculated after the final refinement did not reveal any of the hydrogen atoms around the water oxygens. The atomic coordinates and temperature factors are given in Table 2. All calculations were carried out with the UNIVAC 1108 computer using the X-RAY 76 program system.<sup>7</sup> A listing of structure factors is available from the authors upon request.

Table 1. Crystal data of  $K_2UO_2(SO_4)_2 \cdot 2H_2O$ .

Space group $Pnma$ (No. 62)
$a = 13.806(4)$ , $b = 11.577(1)$ , $c = 7.292(1)$ Å,
$V = 1165.5$ Å <sup>3</sup> ; $Z = 4$ , $D_m = 3.33$ g cm <sup>-3</sup> , <sup>2</sup>
$D_x = 3.284$ g cm <sup>-3</sup> , $\mu(\text{MoK}\alpha) = 185$ cm <sup>-1</sup>

Table 2. Atomic coordinates and temperature factors for  $K_2UO_2(SO_4)_2 \cdot 2H_2O$ . Estimated standard deviations in parentheses. The anisotropic parameters  $U_{ij}$  ( $\text{\AA}^2$ ) are of the form  $\exp(-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23}))$ . All thermal parameters have been multiplied by  $10^2$ .

Atom	x	y	z	$U_{11}$ or $U$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
U	0.7446(1)	0.2500	0.5857(1)	1.06(3)	0.38(3)	0.67(3)	0	-0.03(3)	0
K	0.4298(3)	0.4624(4)	0.2380(6)	1.48(18)	4.43(25)	2.11(19)	0.25(17)	-0.03(16)	0.61(21)
S	0.6761(3)	0.4701(3)	0.2563(6)	1.48(17)	0.80(14)	0.87(15)	0.01(13)	-0.06(14)	0.07(15)
O(1)	0.6173(12)	0.2500	0.6057(25)	1.4(3)					
O(2)	0.8702(12)	0.2500	0.5700(25)	1.4(3)					
O(3)	0.7512(9)	0.4357(9)	0.7095(15)	1.3(2)					
O(4)	0.7405(8)	0.3746(9)	0.3278(15)	1.2(2)					
O(5)	0.6053(10)	0.5109(12)	0.3926(20)	2.3(3)					
O(6)	0.6288(9)	0.4293(11)	0.0875(20)	2.0(2)					
O(7)	0.7369(13)	0.2500	0.9305(25)	1.8(3)					
O(8)	0.4334(19)	0.2500	0.3956(39)	4.2(6)					

Table 3. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ).

Environment of uranium			
U-O(1)	1.768(17)	O(1)-U-O(2)	179.0(8)
U-O(2)	1.744(17)	O(1)-U-O(3)	90.4(4)
U-O(3) ( $\times 2$ )	2.340(11)	O(1)-U-O(4)	92.4(5)
U-O(4) ( $\times 2$ )	2.374(11)	O(1)-U-O(7) <sup>a</sup>	82.9(7)
U-O(7) <sup>a</sup>	2.517(18)	O(2)-U-O(3)	89.2(4)
		O(2)-U-O(4)	88.4(6)
O(3)-U-O(4)	75.2(4)	O(2)-U-O(7) <sup>a</sup>	96.2(7)
O(3)-U-O(7) <sup>a</sup>	67.4(3)		
O(4)-U-O(4')	75.1(4)		
Possible hydrogen bonds			
O(7) <sup>a</sup> -O(6) ( $\times 2$ )	2.809(18)	O(6)-O(7) <sup>a</sup> -O(6')	95.7(7)
Sulfate group			
S-O(6)	1.473(14)	O(3)-S-O(4)	102.3(7)
S-O(5)	1.474(15)	O(4)-S-O(5)	113.3(7)
S-O(4)	1.516(12)	Mean:	109.4 <sup>b</sup>
S-O(3)	1.526(12)		
Mean:	1.497		

<sup>a</sup> Oxygen atom belonging to a water molecule. <sup>b</sup> Mean value of all O-S-O angles.

## RESULTS AND DISCUSSION

The coordination polyhedron around uranium is a pentagonal bipyramid. The equatorial plane contains four oxygen atoms belonging to the sulfate groups, and one oxygen atom of the water molecule. Selected interatomic bond lengths and angles involving uranium and sulfur atoms are given in Table 3. The  $UO_7$ -polyhedra are joined by bridging sulfate groups and form a layer structure normal to the  $a$ -axis (Fig. 1).

One water molecule is not coordinated to uranium, but is located between the layers as well as the potassium atoms which form infinite columns with sulfate groups in the direction of the  $a$ -axis. The formula of the complex may thus be written as  $K_2[UO_2(H_2O)(SO_4)_2] \cdot H_2O$ . Fig. 2 shows the packing arrangement in the lattice as viewed along the  $c$ -axis and Table 4 gives the nearest neighbours of the noncoordinated water molecule and the potassium ion.

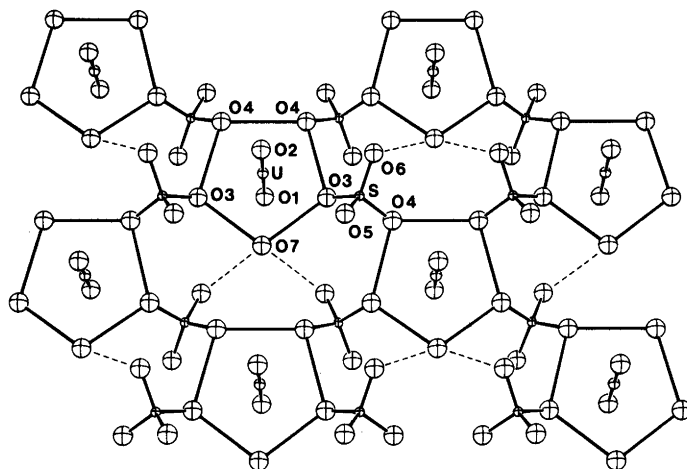


Fig. 1. The  $[\text{UO}_2(\text{H}_2\text{O})(\text{SO}_4)_2]^{2n-}$  layer viewed approximately along the  $a$ -axis. Possible hydrogen bonds are shown as broken lines.

In the linear uranyl group the average U–O bond length, 1.76 Å, is somewhat shorter than the corresponding values of 1.82 and 1.89 Å in  $(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_4\text{UO}_2(\text{SO}_4)_3$ , respectively,<sup>4,8</sup> but comparable to U–O bonds reported for  $\text{UO}_2\text{SO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  and  $\text{UO}_2\text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ .<sup>9,10</sup> The U–O bond lengths in the equatorial plane are in very good agreement with those observed for the ammonium compound, but the pentagon is somewhat more distorted. The deviations from the least-squares plane through the atoms are 0.006 Å for uranium, 0.091 Å and –0.035 Å for the sulfate oxygens O(3) and O(4),

respectively, and –0.118 Å for the water oxygen O(7).

In the sulfate tetrahedron the average S–O distance is slightly longer and the range of O–S–O angles is larger than in the case of  $(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , cf. Table 3 and Ref. 4. There is, however, a similar trend in bond lengths in both compounds, viz. the S–O distances involving oxygens bound to uranium are consistently longer than the free S–O bonds.

The structure shows only a few possibilities for hydrogen bonding. The coordinated water molecule O(7) is probably involved in strengthening the layer

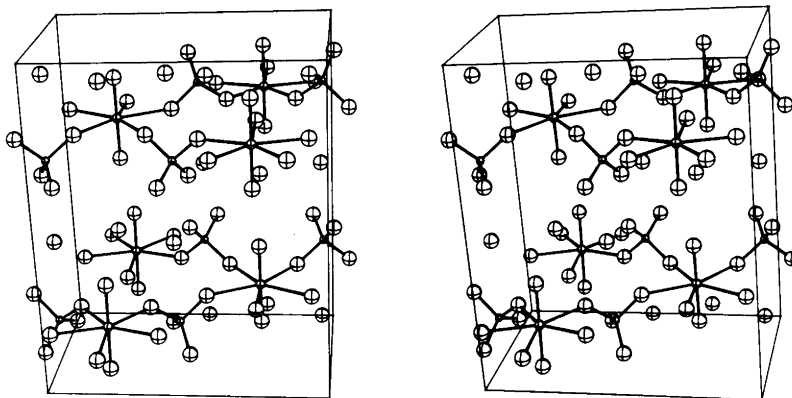


Fig. 2. Stereoscopic view of the packing arrangement of  $\text{K}_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The  $a$ -axis is vertical and the  $b$ -axis is horizontal. The noncoordinated water molecules lie on the mirror planes normal to the  $b$ -axis.

Table 4. The environment of potassium ion and the noncoordinated water (up to 3.2 Å). The superscripts denote the symmetry operations <sup>i</sup>x, y, z, <sup>ii</sup>-x, -y, -z, <sup>iii</sup>x, 1/2-y, z and <sup>iv</sup>1/2+x, y, 1/2-z.

K-O(8) <sup>i</sup>	2.723(13)
K-O(5) <sup>i</sup>	2.738(14)
K-O(5) <sup>ii</sup>	2.755(15)
K-O(3) <sup>ii</sup>	2.798(13)
K-O(6) <sup>ii</sup>	2.807(15)
K-O(4) <sup>iv</sup>	2.852(12)
K-O(6) <sup>i</sup>	2.991(13)
O(8)-K <sup>i,iii</sup> (×2)	2.723(13)
O(8)-O(1) <sup>i</sup>	2.973(32)
O(8)-O(7) <sup>iv</sup>	3.001(32)

structure through hydrogen bonding to opposite sulfate oxygens (Table 3 and Fig. 1). The same type of bonding has been observed in the structure of  $\text{UO}_2(\text{CH}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$  where the packing of the  $\text{UO}_7$ -polyhedra and the methanesulfonate tetrahedra is similar.<sup>11</sup> Although the arrangement of the building units is different in  $(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , there are also, in this case, hydrogen bonds crossing the gaps within the layer.

It is likely that the other water molecule O(8), located between the layers, is also involved in hydrogen bonding because it has two contacts of 2.97 and 3.00 Å to O(1) and O(7), respectively, and the angle O(1)-O(8)-O(7) is 123.9(11)°. O(8) is also part of the coordination sphere of potassium ion which has, in addition, six sulfate oxygens at distances less than 3.0 Å (Table 4). The average K-O distance is 2.81 Å.

When comparing the present structure to that of  $(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , it may be noted that both compounds have a similar layer structure but in the case of  $\text{K}_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  the basic building unit is a single  $\text{UO}_7$ -polyhedron while the layers in the structure of  $(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  contain two symmetry-related polyhedra joined together by two sulfate groups. In both cases the layers are tied together in the third dimension by the noncoordinated water molecules and the monovalent cations. The distances between the layers, as determined from the least-squares planes through uranium atoms, are of the same order of magnitude, viz. 6.71 and 6.90 Å for  $(\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_2\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , respectively.

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