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Uranyl(VI) Compounds. I. The Crystal Structure of Ammonium Uranyl Sulfate Dihydrate, $(NH_4)_2UO_2(SO_4)_2.2H_2O$

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The crystal structure of $(NH_4)_2UO_2(SO_4)_2.2H_2O$ has been determined by single crystal X-ray diffraction techniques. The compound crystallizes in the space group $P2_1/c$ with unit cell dimensions $a=7.783(5)$, $b=7.403(2)$, $c=20.918(9)$ Å, $\beta=102.25(4)°$, and $Z=4$. Least-squares refinement with anisotropic temperature factors for the uranium and sulfur atoms resulted in an R-value of 0.053 for 2251 significant reflections. The coordination polyhedron around uranium is a pentagonal bipyramid. Sulfate groups join the polyhedra into a layered structure where the ammonium ions and half of the water molecules are located between the layers. The mean bond lengths are: U–O(uranyl)=1.82, U–O(sulfate)=2.36, and U–O(water)=2.52 Å. The IR spectrum of the compound has also been recorded and interpreted.

Uranyl compounds, including the sulfates, have received considerable attention during recent years. Thus, the structures of normal sulfates, $UO_2SO_4.2\frac{1}{2}H_2O$ and $UO_2SO_4.3\frac{1}{2}H_2O$,[1,2] as well as of the complex ones, $Cs_2(UO_2)_2(SO_4)_3$ and $K_4UO_2(SO_4)_3$,[3,4] have been determined by X-ray diffraction methods. The results indicate that although the coordination polyhedron around uranium in the sulfate structures is invariably a pentagonal bipyramid, the polyhedra may be linked together in three dimensions quite differently.

The present work was initiated as part of a systematic study on the structures and spectroscopic and thermal properties of the complex uranium sulfates. The ammonium compound $(NH_4)_2UO_2(SO_4)_2.2H_2O$ was chosen for single crystal structure analysis because its stoichiometry corresponds to the complex anion $[UO_2(SO_4)_2]^{2-}$; although determined as one of the main species in solution,[5] this anion has not previously been structurally characterized in the solid state. Another interesting feature of this compound is the role of water molecules in the structure as compared with the anhydrous $Cs_2(UO_2)_2(SO_4)_3$ and $K_4UO_2(SO_4)_3$.

EXPERIMENTAL

The compound was crystallized at room temperature from an aqueous solution containing ammonium and uranyl sulfates in equimolar amounts.[6] The yellow crystals, strongly fluorescent in UV-light, corresponded well to the description given by Traill.[7] The crystal data are summarized in Table 1. The unit cell is given here in the standard setting ($P2_1/c$); another choice would be $P2_1/n$.[7]

The single crystal intensity data in the interval $5°<2\theta<60°$ were collected with a Syntex $P2_1$ (Fortran version) automatic diffractometer, using the $\theta/2\theta$ technique and graphite monochromatized Mo$K\alpha$-radiation. The scan speed was 1°/min. The crystal had approximate dimensions $0.3\times0.1\times0.1$ mm. A total of 2251 independent reflections satisfying the criterion $I>3\sigma(I)$ were used in the subsequent calculations. The intensities were corrected for Lorentz and polarization effects and for absorption from the ϕ-scan data.

A three-dimensional Patterson function revealed the position of the uranium atom and its coordinates

Table 1. Crystal data of $(NH_4)_2UO_2(SO_4)_2.2H_2O$.

Space group $P2_1/c$ (No. 14)
$a=7.783(5)$, $b=7.403(2)$, $c=20.918(9)$ Å,
$\beta=102.25(4)°$, $V=1177.8$ Å^3,[a] $Z=4$, $D_m=3.0$ g cm^{-3}, $D_x=3.01$ g cm^{-3}, μ(Mo$K\alpha$)=135 cm^{-1}

[a] Diffractometer data at 25 °C based on 25 reflections. Mo$K\alpha$-radiation ($\lambda=0.7107$ Å).

Table 2. Atomic coordinates and temperature factors for $(NH_4)_2UO_2(SO_4)_2.2H_2O$. Estimated standard deviations have been given in parentheses. The anisotropic parameters U_{ij} (Å^2) are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2klb^*c^*U_{23})]$. 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	0.2306(1)	0.3892(1)	0.3772(1)	1.07(2)	1.36(2)	1.12(3)	−0.08(2)	0.06(2)	−0.01(2)
S(1)	0.5489(5)	0.7161(5)	0.4545(2)	1.50(15)	1.39(16)	1.37(21)	−0.13(13)	0.14(13)	0.02(13)
S(2)	0.1432(5)	0.7270(6)	0.2477(2)	2.32(18)	1.76(17)	1.46(22)	0.18(15)	−0.06(15)	0.20(15)
O(1)	0.4144(16)	0.3612(17)	0.3371(6)	2.4(3)					
O(2)	0.0423(15)	0.4176(16)	0.4151(6)	2.2(2)					
O(3)	0.4009(16)	0.2562(18)	0.4741(6)	2.5(3)					
O(4)	0.3690(16)	0.6325(17)	0.4400(6)	2.3(3)					
O(5)	0.5350(16)	0.8914(19)	0.4222(6)	2.6(3)					
O(6)	0.6770(17)	0.5984(19)	0.4316(7)	2.8(3)					
O(7)	0.1381(17)	0.6475(18)	0.3127(7)	2.9(3)					
O(8)	0.0437(17)	0.2750(18)	0.2831(7)	2.7(3)					
O(9)	0.2097(21)	0.5977(24)	0.2068(8)	4.2(4)					
O(10)	0.2453(19)	0.8926(22)	0.2598(7)	3.7(3)					
O(11)	0.2205(17)	0.0495(16)	0.3774(7)	2.3(2)					
O(12)	0.7598(23)	0.1996(23)	0.4336(9)	4.5(4)					
N(1)	0.6517(27)	0.7293(29)	0.2964(10)	4.4(5)					
N(2)	0.9788(26)	0.8422(26)	0.4455(10)	4.1(4)					

Table 3. Selected interatomic distances (Å) and angles (°).

Environment of uranium			
U−O(1)	1.818(14)	O(1)−U−O(2)	178.3(5)
−O(2)	1.819(13)	O(1)−U−O(3)	89.7(5)
Mean	1.819	O(1)−U−O(4)	91.9(5)
		O(1)−U−O(7)	90.2(5)
U−O(8)	2.344(13)	O(1)−U−O(8)	88.9(5)
−O(4)	2.351(12)	O(1)−U−O(11)[a]	85.1(5)
−O(7)	2.364(14)	O(2)−U−O(3)	91.8(5)
−O(3)	2.385(12)	O(2)−U−O(4)	89.1(5)
−O(11)[a]	2.516(12)	O(2)−U−O(7)	88.8(5)
Mean	2.392	O(2)−U−O(8)	89.6(5)
		O(2)−U−O(11)[a]	95.0(5)
O(3)−U−O(4)	74.7(4)		
O(4)−U−O(7)	75.4(4)	Possible hydrogen bonds	
O(7)−U−O(8)	75.7(5)	O(11)[a]−O(5)	2.695(18)
O(8)−U−O(11)[a]	68.1(4)	−O(10)	2.765(21)
O(11)[a]−U−O(3)	66.3(4)	O(5)−O(11)[a]−O(10)	84.1(6)
Sulfate groups			
S(1)−O(5)	1.457(14)	S(2)−O(9)	1.450(19)
−O(3)	1.477(14)	−O(10)	1.453(17)
−O(6)	1.478(15)	−O(7)	1.489(15)
−O(4)	1.501(13)	−O(8)	1.503(13)
Mean:	1.478	Mean:	1.474
O(4)−S(1)−O(3)	107.3(8)	O(7)−S(2)−O(8)	105.9(8)
O(5)−S(1)−O(6)	111.4(8)	O(9)−S(2)−O(10)	114.1(10)
Mean:	109.4[b]	Mean:	109.2[b]

[a] Oxygen atom belonging to a water molecule. [b] Mean value of all O−S−O angles.

were refined. The subsequent electron density map showed the positions of all the remaining non-hydrogen atoms.

A block-diagonal least-squares refinement with anisotropic temperature factors for uranium and sulfur led to the final value of 0.053 for the conventional R index; the weighted R index was 0.072 $[w=1/\sigma^2(F_o^2)]$. In the refinement scattering fractors for neutral atoms were used, and, for uranium, a correction for the anomalous scattering was applied.[8] It was not possible to locate any of the hydrogen atoms from a difference Fourier map calculated after the final refinement.

All calculations were performed with the UNIVAC 1108 computer using the X-RAY 76 program system.[9] A listing of structure factors is available from the authors upon request.

The infrared spectrum in the range 4000–250 cm^{-1} was recorded on a Perkin-Elmer 521 spectrophotometer with the KBr pellet technique. The compound showed no reaction with KBr.

DESCRIPTION AND DISCUSSION OF STRUCTURE

The atomic coordinates and temperature factors are given in Table 2. Selected interatomic bond lengths and angles involving uranium and sulfur atoms are given in Table 3.

The coordination polyhedron around uranium is, as expected, a pentagonal bipyramid. Our X-ray data are in full agreement with the linearity and symmetry of the uranyl group (Table 3) and also with the nearly planar arrangement of uranium and the five equatorial oxygens (Table 4).

Table 4. Deviations of atoms (Å) from the least-squares plane.

Atom	Deviation (Å)
U	−0.027
O(3)	−0.031
O(4)	0.006
O(7)	0.040
O(8)	−0.053
O(11)	0.065

The UO_7-polyhedra are joined into a layer structure by sulfate groups (Fig. 1). The basic building unit of the structure consists of two symmetry-related UO_7-polyhedra joined together by $S(1)O_4$ tetrahedra. These double polyhedra are connected by $S(2)O_4$ bridging groups into an infinite layer $[UO_2(H_2O)(SO_4)_2]_n^{2n-}$.

The sulfate tetrahedra are not significantly distorted in this process although S–O distances involving oxygens bonded to uranium are generally slightly longer than the free S–O bonds. In the coordination polyhedron of uranium, however, the U–O(sulfate) distances are significantly shorter than the U–O(water) distance. The water molecule O(11) is probably involved in strengthening the layer structure through hydrogen bonding to neighbouring sulfate oxygens O(5) and O(10); this

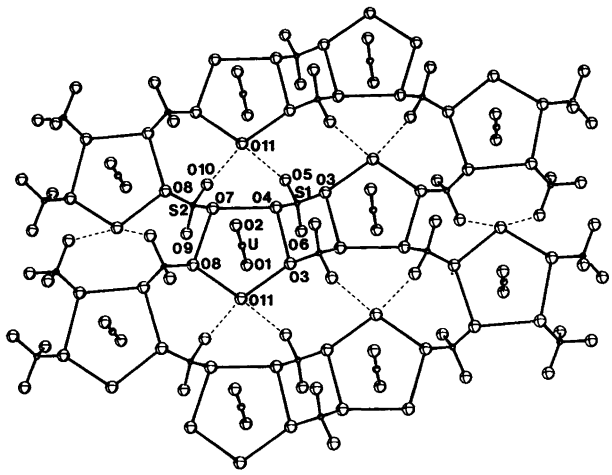

Fig. 1. The $[UO_2(H_2O)(SO_4)_2]_n^{2n-}$ layer viewed roughly perpendicular to the equatorial plane of the UO_7-polyhedra. Possible hydrogen bonds are shown as broken lines.

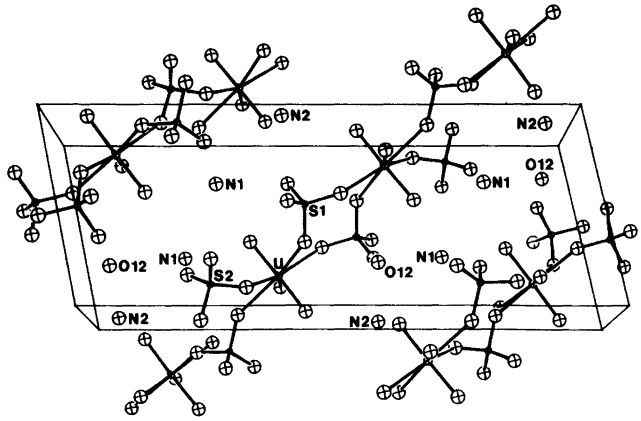

Fig. 2. A perspective view showing the unit cell contents of $(NH_4)_2UO_2(SO_4)_2.2H_2O$. The *a*-axis is vertical and the *c*-axis is horizontal.

may cause the difference in bond lengths (*cf.* Table 3 and Fig. 1).

Half of the water molecules and the ammonium ions do not form part of the layers but are located between them and joined to the structure probably by hydrogen bonding (Fig. 2). Table 5 gives the nearest neighbours of these atoms. Possible hydrogen bonds for the water molecule O(12) are also suggested in this table.

Table 5. The environment of ammonium ions and the noncoordinated water molecule (up to 3.2 Å).

N(1)–O(1)^{ii} [a]	2.900(25)
–O(9)^{ii}	2.939(28)
–O(10)^{ii}	2.939(28)
–O(6)	2.956(26)
–O(8)^{ii}	3.190(28)
–O(5)	3.194(27)
N(2)–O(12)^{i}	2.907(24)
–O(6)	2.928(24)
–O(11)	3.009(26)
–O(12)	3.128(27)
O(12)–O(2)	2.820(22)
–O(5)	2.854(22)
–O(6)	3.021(22)
–O(9)^{ii}	3.089(26)
–O(3)	3.115(24)
O(6)–O(12)–O(9) (°)	106.6(7)

[a] The superscripts denote the symmetry operations: ^{i} $-x,-y,-z$ and ^{ii} $-x,1/2+y,1/2-z$.

There are several possible hydrogen bond acceptors for the ammonium ions at distances less than 3.2 Å. However, the angles calculated at both N(1) and N(2) are not acceptable for a regular

Table 6. Infrared absorption frequencies in the region 4000–400 cm^{-1}.

Observed frequency	Assignment
3600 m, 3500 m	$\nu(H_2O)$
3175 vs	$\nu_3(NH_4)$
3000 sh	$\nu_1(NH_4)$
2850 m	$2\nu_4(NH_4)$
1990 w	$2\nu_1(SO_4)$
1620 m, 1595 m	$\delta(H_2O)$
1425 s	$\nu_4(NH_4)$
1205 s, 1165 sh, 1120 vs, 1060 s, 1020 sh	$\nu_3(SO_4)$
990 vs	$\nu_1(SO_4)$
924 s	$\nu_3(UO_2)$
836 m	$\nu_1(UO_2)$
640 m, 610 m, 590 sh, 580 s	$\nu_4(SO_4)$
470 w, 455 w, 435 w, 425 sh	$\nu_2(SO_4)$

hydrogen bonding scheme. Thus, it seems probable that the ammonium ions are in static or dynamic disorder.[10]

THE INFRARED SPECTRUM

The IR spectrum of $(NH_4)_2UO_2(SO_4)_2.2H_2O$ was recorded and interpreted in this work (Table 6). Narasimham and Girija earlier studied the same compound by absorption spectroscopy but their main emphasis was on the uranyl group.[11]

On the basis of the IR spectrum it is possible to deduce some of the main features of the structure: (i) the splitting of sulfate ν_3 and ν_4 vibrations into three peaks indicates C_{2v} symmetry for the sulfate group (bidentate ligand, bridging or chelate), and (ii) the splitting of the bending vibration of H_2O around 1600 cm^{-1} indicates two types of water molecules in the structure.

Further structural conclusions based on the IR spectrum alone are not warranted until the absorption spectra of a larger number of uranyl sulfates have been compared with the X-ray diffraction results.

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REFERENCES

1. Putten, N. and Loopstra, B. O. *Cryst. Struct. Commun. 3* (1974) 377.
2. Brandenburg, N. P. and Loopstra, B. O. *Cryst. Struct. Commun. 2* (1973) 243.
3. Ross, M. and Evans, H. T. *J. Inorg. Nucl. Chem. 15* (1960) 338.
4. Mikhailov, Yu. N., Kokh, L. A., Kuznetsov, V. G., Grevtseva, T. G., Sokol, S. K. and Ellert, G. V. *Koord. Khim. 3* (1977) 508.
5. Ahrland, S. *Acta Chem. Scand. 5* (1951) 1151.
6. Colani, A. *Bull. Soc. Chim. Fr. 43* (1928) 754.
7. Traill, R. J. *Am. Mineral. 37* (1952) 394.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4, pp. 71, 150.
9. Stewart, J. M., Ed., *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park.
10. Khan, A. A. and Bauer, W. H. *Acta Crystallogr. B 28* (1972) 693.
11. Narasimham, K. V. and Girija, M. *Indian J. Pure Appl. Phys. 6* (1968) 231.

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