ethyldithiocarbamate) anion,[17] and an average value of 2.84 Å found in the triphenylphosphine oxide and triphenylarsine oxide adducts of uranyl diethyldithiocarbamate.[18]

Three types of U–O distances are found in this structure; they are the uranyl-, ethoxide-, and carbamate-type bonds with distances of 1.78, 2.20, and 2.39 Å, respectively.

Registry No. $(C_2H_5)_2NH_2^+[UO_2((C_2H_5)_2HCOS)_2OC_2H_5]^-$, 67827-33-2.

Supplementary Material Available: Data processing formulas and the listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Structure of a New Uranyl Sulfate Hydrate, α-$2UO_2SO_4{\cdot}7H_2O$[1]

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Received June 9, 1978

When an aqueous solution of uranyl sulfate and (+)-tartaric acid was allowed to evaporate slowly, white crystals of tartaric acid and yellow crystals of a new uranyl sulfate hydrate both came out of solution. The X-ray crystal structure determination reported in this paper established that the yellow crystals are $2UO_2SO_4{\cdot}7H_2O$ with identical composition but different structure than a previously reported "metastable hydrate"[2,3] of uranyl sulfate; this latter compound will be referred to here as β-$2UO_2SO_4{\cdot}7H_2O$. The α-form crystal used for this study is air stable and showed no evidence of decomposition during the 4 weeks it was being studied and exposed to X-rays.

Experimental Section

An irregular wedge-shaped crystal with approximate dimensions 0.30 × 0.11 × 0.15 mm was glued to a glass fiber and examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of the 600, 040, and 006 reflections showed half-widths of 0.15, 0.11, and 0.09°, respectively. Absent reflections indicated space groups *Pmca* or $P2_1ca$; the subsequent Patterson function indicated two different uranium atoms which could only be accommodated in the noncentric space group $P2_1ca$.[4] The setting angles of 12 manually centered reflections (40° < 2θ < 50°) were used to determine by least squares the cell parameters a = 11.227 (6) Å, b = 6.790 (3) Å, c = 21.186 (10) Å, and V = 1615 Å^3. For Z = 4 and a molecular weight of 858.29 the calculated density is 3.53 g/cm^3; the calculated density of the β form is 3.46 g/cm^3. No extinction correction was indicated nor applied.

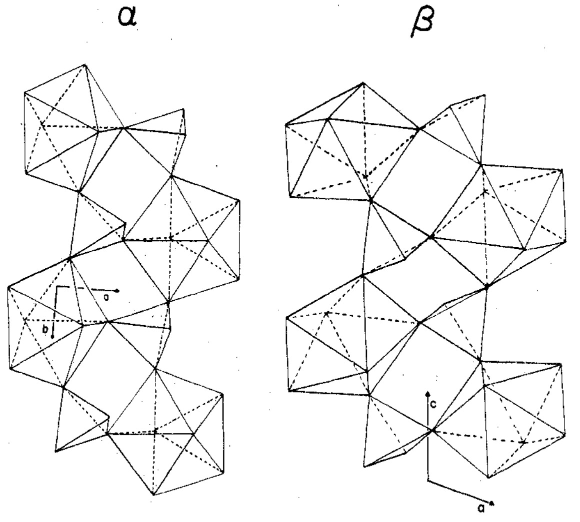

Figure 1. Comparison of the arrangement in the α and β forms of $2UO_2SO_4{\cdot}7H_2O$.

Intensity data were collected using the θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each reflection was scanned from 0.75° before the $K\alpha_1$ peak to 0.75° after the $K\alpha_2$ peak, and backgrounds were counted for 4 s at each end of the scan range, offset by 0.5°. The temperature during data collection was 21 ± 1 °C. Three standard reflections were measured after every 200th scan. The 6177 scans, not including standards, resulted in 5640 unique intensities in which the Friedel pairs were not averaged. The data were corrected for absorption by an analytical method[5] using an estimated absorption coefficient of 193 cm^{-1}; absorption corrections varied from 4.8 to 10.0.

A three-dimensional Patterson function calculation revealed two crystallographically unique uranium atoms, each in the general position. Subsequent least-squares calculations and Fourier maps revealed the positions of all of the light atoms. A series of least squares in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized converged rapidly to the final structure. The expressions that were used in processing the data and estimating the weights are given in the supplementary material; the "ignorance factor", p, was set to 0.05. Scattering factors from Doyle and Turner[6] were used, and anomalous dispersion corrections[7] were applied. When f'' of uranium was treated as a variable as described elsewhere,[8] it refined to 9.4 ± 0.3, within 1σ of the literature[7] value. This result shows that the absolute orientation of the structure was chosen correctly and that the specimen was substantially free of inversion twinning. The positions of all of the hydrogen atoms were estimated from the hydrogen bonding and were included in the calculation of the structure factors but not refined. Anisotropic thermal parameters were included only for uranium. No extinction correction was indicated nor applied. The discrepancy indices for 3437 data (Friedel pairs not averaged) where $F^2 > 3\sigma$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.049$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.054$$

R for all 5640 data is 0.103. The error in an observation of unit weight is 1.24. In the last cycle no parameter changed more than 0.07σ.

Results and Discussion

Atomic parameters, distances, and angles are listed in Tables I–III. The uranium atom is at the center of a pentagonal bipyramid arrangement of oxygen atoms. These are joined in an infinite chain along the b axis by sulfate tetrahedra as is shown in Figure 1. The β form also contains chains made

0020-1669/78/1317-3701$01.00/0

Table I. Positional and Thermal Parameters[a] with Estimated Standard Deviations[b] for α-$2UO_2SO_4\cdot 7H_2O$

atom	x	y	z	B, Å^2
U(1)	0	0.19112 (9)	0.07967 (3)	
U(2)	0.38767 (7)	0.70137 (9)	0.20043 (3)	
S(1)	0.1164 (3)	0.6890 (7)	0.1033 (2)	1.23 (6)
S(2)	0.2961 (4)	0.1933 (8)	0.1512 (2)	1.49 (6)
O(1)	−0.095 (1)	0.184 (2)	0.1451 (6)	3.6 (2)
O(2)	0.089 (1)	0.189 (2)	0.0113 (7)	3.6 (2)
O(3)	0.451 (1)	0.703 (2)	0.1239 (7)	3.6 (2)
O(4)	0.326 (1)	0.705 (2)	0.2758 (7)	3.3 (2)
O(5)	0.043 (1)	0.514 (2)	0.1194 (7)	3.0 (2)
O(6)	0.188 (1)	0.734 (2)	0.1604 (6)	3.0 (2)
O(7)	0.189 (1)	0.647 (3)	0.0492 (9)	4.6 (3)
O(8)	0.030 (1)	0.850 (2)	0.0940 (7)	3.8 (3)
O(9)	0.318 (1)	0.382 (2)	0.1826 (8)	4.0 (3)
O(10)	0.341 (1)	0.039 (2)	0.1947 (7)	3.3 (2)
O(11)	0.352 (1)	0.190 (3)	0.0904 (8)	4.5 (3)
O(12)	0.164 (1)	0.167 (2)	0.1467 (6)	3.2 (2)
O(13)	0.534 (1)	0.483 (2)	0.2460 (7)	3.3 (2)
O(14)	−0.126 (1)	0.439 (2)	0.0274 (7)	4.1 (3)
O(15)	0.656 (2)	0.204 (3)	0.1869 (9)	4.8 (3)
O(16)	−0.155 (1)	0.020 (2)	0.0223 (7)	3.4 (2)
O(17)	0.556 (1)	0.892 (2)	0.2368 (7)	3.4 (2)
O(18)	0.595 (2)	0.290 (4)	0.073 (1)	8.3 (6)
O(19)	0.248 (2)	0.725 (3)	0.4069 (9)	4.6 (3)
H(1)	0.5376	0.4933	0.291	*c*
H(2)	0.5749	0.3904	0.2263	
H(3)	−0.1889	0.4109	0.0021	
H(4)	−0.1691	0.5349	0.0496	
H(5)	0.7386	0.1982	0.1726	
H(6)	0.636	0.2337	0.1481	
H(7)	−0.1522	−0.0499	−0.0155	
H(8)	−0.1857	−0.0787	0.0458	
H(9)	0.6006	0.8398	0.271	
H(10)	0.5901	0.9967	0.2199	
H(11)	0.6272	0.3111	0.0313	
H(12)	0.5154	0.2564	0.0777	
H(13)	0.1952	0.7538	0.4414	
H(14)	0.2741	0.7182	0.3629	

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U(1)	1.05 (2)	0.98 (2)	1.54 (2)	0.01 (4)	−0.27 (2)	−0.01 (2)
U(2)	0.95 (2)	0.95 (2)	1.51 (2)	0.03 (4)	−0.18 (2)	−0.02 (2)

[a] The anisotropic temperature factor has the form $\exp(-0.25\cdot(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots))$. [b] Here and in the following tables the numbers in parentheses are the estimated standard deviations in the least significant digit. [c] Hydrogen positions were estimated and not refined. An arbitrary isotropic thermal parameter of 6.0 Å^2 was assigned to each of the hydrogen atoms.

Table II. Selected Interatomic Distances (Å)

U(1)-O(1)	1.75 (2)	U(2)-O(3)	1.77 (2)
-O(2)	1.76 (2)	-O(4)	1.74 (2)
-O(5)	2.40 (2)	-O(6)	2.41 (2)
-O(8)	2.36 (2)	-O(9)	2.34 (2)
-O(12)	2.33 (2)	-O(10)	2.36 (2)
-O(14)	2.47 (2)	-O(13)	2.41 (2)
-O(16)	2.42 (2)	-O(17)	2.41 (2)
S(1)-O(5)	1.49 (2)	S(2)-O(9)	1.46 (2)
-O(6)	1.48 (2)	-O(10)	1.48 (2)
-O(7)	1.44 (2)	-O(11)	1.44 (2)
-O(8)	1.47 (2)	-O(12)	1.50 (2)

up of very similar units of two bipyramids and two tetrahedra, as shown also in Figure 1 for comparison. The overall structures of these chains are different; in the chain in the α form the units are repeated according to the b-axis translation, while in the β form the replication is by a glide plane. As a result, alternate units in the latter case have reversed orientations. The interatomic distances and angles are comparable in the two forms.[2] The molecular volume is 2% smaller in the α form indicating a very slightly more efficient packing.

Table III. Hydrogen Bond Distances and Angles

atoms	distances, Å		angle, deg
O(5)-O(13)-O(15)	2.86 (2)	2.65 (3)	120 (1)
O(7)-O(14)-O(19)	2.70 (3)	2.77 (2)	94 (1)
O(1)-O(15)-O(18)	2.94 (3)	2.58 (3)	89 (1)
O(11)-O(16)-O(19)	2.78 (3)	2.73 (3)	96 (1)
O(6)-O(17)-O(15)	2.84 (2)	2.62 (3)	113 (1)
O(7)-O(18)-O(11)	2.83 (4)	2.83 (4)	121 (1)
O(2)-O(19)-O(4)	2.90 (3)	2.92 (3)	157 (1)

All the water molecules are hydrogen bonded, and distances and angles for these bonds are listed in Table III.

Acknowledgment. We thank Dr. L. K. Templeton for assistance with the refinement of f''.

Registry No. α-$2UO_2SO_4\cdot 7H_2O$, 39448-26-5.

Supplementary Material Available: Data processing formulas, table of angles, and the listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

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(4) $P2_1ca$ is a nonstandard description of $Pca2_1$. Equivalent positions for $P2_1ca$: x, y, z; $^1/_2 + x, -y, -z$; $x, -y, ^1/_2 + z$; $^1/_2 + x, y, ^1/_2 - z$.

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Crystal Structure of Tetrakis(2,2′-bipyridine dioxide)lanthanum Perchlorate: An Example of Cubic Eight-Coordination

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Received August 4, 1978

On the basis of ligand–ligand repulsions the cube is expected to be a much less favorable coordination geometry for discrete eight-coordinate complexes than the dodecahedron (D_{2d}) or the square antiprism (D_{4d}), for both of which structurally characterized examples abound in the literature.[1] However, of the comparatively few examples of ML_8 stoichiometry (L = unidentate ligand) whose structures have been determined, two of these in fact have cubic geometry, namely, PaF_8^{3-}[2] and $U(NCS)_8^{4-}$[3] in the form of its tetraethylammonium salt. The latter complex ion is of interest, for in the cesium salt it adopts the square-antiprismatic geometry[4] suggesting that the counterion and crystal-packing arrangement may dictate the geometry and that cubic eight-coordination may not be that unfavorable, at least for the heavier elements. Approximately cubic geometry is also apparently found in another complex of uranium, namely, tetrakis(bipyridyl)uranium,[5] and we have found for the octakis(pyridine N-oxide) complexes of the lighter lanthanides $Ln(pyO)_8^{3+}$ that while in one of the crystalline forms the complex ions have a square-antiprismatic geometry, in a second form the coordination polyhedron is distorted from the D_{4d} geometry toward that of a cube, rather

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