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β -Uranyl Sulphate and Uranyl Selenate

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Abstract. β - UO_2SO_4 , monoclinic, $P2_1/c$, $a = 6.760$ (1), $b = 5.711$ (1), $c = 12.824$ (4) Å, $\beta = 102.91$ (2)°, $V = 482.6$ Å³, $Z = 4$, $D_c = 5.04$ g cm⁻³. α - UO_2SeO_4 , monoclinic, $P2_1/c$, $a = 6.909$ (1), $b = 5.525$ (1), $c = 13.318$ (3) Å, $\beta = 103.79$ (2)°, $V = 493.7$ Å³, $Z = 4$, $D_c = 5.569$ g cm⁻³. β - UO_2SeO_4 , monoclinic, $P2_1/c$, $a = 6.979$ (1), $b = 5.795$ (1), $c = 13.235$ (2) Å, $\beta = 103.71$ (2)°, $V = 520.0$ Å³, $Z = 4$, $D_c = 5.279$ g cm⁻³. The structures of the isostructural title compounds have been solved from X-ray and neutron diffraction powder data. U atoms are coordinated by pentagonal bipyramids of O atoms. Remarkably, a uranyl O atom of one bipyramid belongs to the pentagonal base plane of the next.

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Table 1. Coordinates and thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
(a) For β - UO_2SO_4				
U	0.315 (1)	0.744 (1)	0.658 (1)	1.3 (2)
S	0.209 (4)	0.454 (5)	0.888 (2)	2.7 (7)
O(1)	0.612 (2)	0.789 (2)	0.592 (1)	1.5 (2)
O(2)	0.220 (2)	0.954 (2)	0.502 (1)	1.5 (2)
O(3)	-0.028 (2)	0.816 (2)	0.643 (1)	1.5 (2)
O(4)	0.241 (2)	0.632 (2)	0.822 (1)	1.5 (2)
O(5)	0.604 (2)	0.514 (3)	0.774 (1)	1.5 (2)
O(6)	0.254 (2)	0.478 (2)	0.595 (1)	1.5 (2)
(b) For α - UO_2SeO_4				
U	0.338 (2)	0.709 (2)	0.648 (1)	1.2 (4)
Se	0.201 (2)	0.440 (3)	0.887 (1)	1.3 (5)
O(1)	0.650 (3)	0.711 (3)	0.613 (1)	1.4 (3)
O(2)	0.300 (2)	0.878 (4)	0.484 (1)	1.4 (3)
O(3)	0.016 (3)	0.852 (4)	0.600 (1)	1.4 (3)
O(4)	0.175 (2)	0.598 (4)	0.781 (1)	1.4 (3)
O(5)	0.581 (2)	0.484 (4)	0.784 (1)	1.4 (3)
O(6)	0.266 (2)	0.422 (4)	0.590 (1)	1.4 (3)

Introduction. The structure determinations were undertaken in connection with thermochemical investigations on uranyl salts of oxyacids containing Group VI elements (Brandenburg, 1978; Cordfunke & Ouweltjes, 1977).

β - UO_2SO_4

Anhydrous β - UO_2SO_4 was prepared by dehydration of $\text{UO}_2\text{SO}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$ (Cordfunke, 1969) in air at 500°C. Analysis gave U: 65.07% (calc. 65.02%). Neutron powder data were collected at the HFR in Petten [0.02

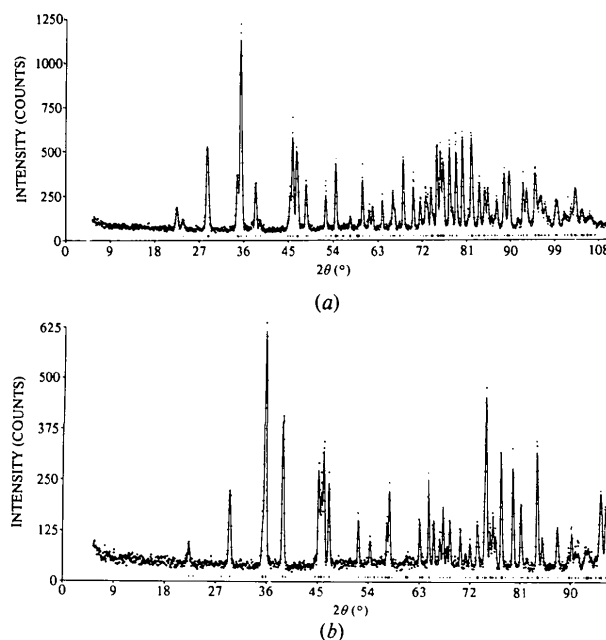


Fig. 1. Observed and calculated neutron powder pattern of (a) β - UO_2SO_4 , (b) α - UO_2SeO_4 . Full line: calculated profile; dots: measurements.

$< (\sin \theta)/\lambda < 0.36 \text{ \AA}^{-1}$, step $0.072^\circ 2\theta$, $\lambda = 2.572 \text{ \AA}$, cylindrical sample $\phi = 10 \text{ mm}$, $10'$ Soller slits between reactor and monochromator, and in front of the BF_3 detector]. Cell constants were taken from Cordfunke (1972). Starting from the coordinates of the isostructural $\alpha\text{-UO}_2\text{SeO}_4$ (Table 1*b*), the determination was carried out with the neutron data. The final R was 0.080. Coordinates and thermal parameters are listed in Table 1(*a*), selected bond lengths and angles in Table 2. Fig. 1(*a*) shows the fit of calculated and observed powder patterns, Fig. 2(*a*) the structure projected along the b axis.

$\alpha\text{-UO}_2\text{SeO}_4$

Hydrated UO_2SeO_4 was prepared by dissolving UO_3 in a warm solution of H_2SeO_4 until saturation. After evaporation the viscous residue was heated to 200°C in air to obtain anhydrous UO_2SeO_4 . Analysis gave U: 57.84% (calc. 57.64%); Se: 19.0% (calc. 19.12%). Step-scanned X-ray powder data were collected on a Philips PW 1150 diffractometer [$0.06 < (\sin \theta)/\lambda < 0.41 \text{ \AA}^{-1}$, Cu $K\alpha$, step $0.02^\circ 2\theta$]. Neutron powder data were collected as described for $\beta\text{-UO}_2\text{SO}_4$ ($\lambda = 2.574 \text{ \AA}$). Indexing of the powder pattern was performed from Cu $K\alpha$ Guinier film data (internal standard: α -quartz). The indexing program written by Visser (1969) led to the cell constants. Reflections $0k0$ with $k = 2n + 1$ and $h0l$ with $l = 2n + 1$ were absent. From

the X-ray intensities, separated into single reflections as circumstances permitted, a 56-term Patterson function was calculated. As reflections with $l = 2n$ are systematically stronger than those with $l = 2n + 1$, the U atom must be in or close to the glide plane at $y = \frac{1}{4}$. From the Harker peaks two possible U positions were found: U either at 0.35, 0.75, 0.65 or at 0.35, 0.75, 0.90. Packing considerations, based on the assumption that the O atom polyhedra around the U are pentagonal bipyramids, led to the correct trial structure. Refinement was achieved with Rietveld's (1969) profile-fitting program applied to the neutron data, keeping a common temperature factor for the O atoms. Final R , as defined by Rietveld (1969): 0.064. Table 1(*b*) lists the final positional and temperature parameters; selected bond lengths and angles are listed in Table 2. Fig. 1(*b*) shows the fit of calculated and observed powder patterns, Fig. 2(*b*) the structure projected along the b axis.

$\beta\text{-UO}_2\text{SeO}_4$

This substance is obtained from $\alpha\text{-UO}_2\text{SeO}_4$ by a reversible transition at about 300°C . From a high-temperature Guinier film α - and $\beta\text{-UO}_2\text{SeO}_4$ are seen to be isostructural. Comparison of the axial ratios of $\beta\text{-UO}_2\text{SO}_4$ ($c/a = 1.897$, $c/b = 2.245$), $\alpha\text{-UO}_2\text{SeO}_4$ (1.928, 2.410) and $\beta\text{-UO}_2\text{SeO}_4$ (1.896, 2.284) indicates a very close analogy between $\beta\text{-UO}_2\text{SO}_4$ and $\beta\text{-UO}_2\text{SeO}_4$. Hence no further structure determination of $\beta\text{-UO}_2\text{SeO}_4$ was undertaken.

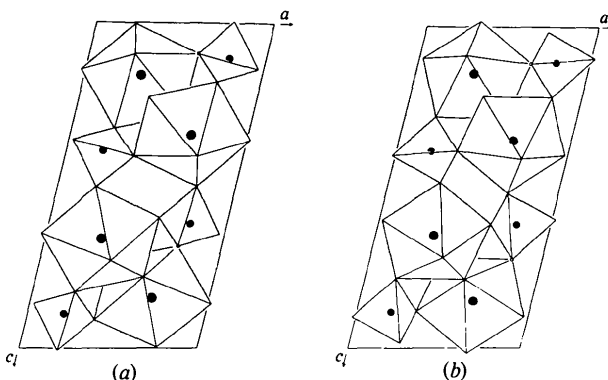


Fig. 2. Structure projected along b of (a) $\beta\text{-UO}_2\text{SO}_4$, (b) $\alpha\text{-UO}_2\text{SeO}_4$. Coordination polyhedra are shown of U (large dots) and S/Se (small dots).

Discussion. The structures of the title compounds consist of infinite chains along b of pentagonal bipyramidal O atom polyhedra around the U atoms. In the chains the linkage is as shown in Fig. 3, a uranyl O atom of one group belonging to the pentagonal base plane of the next. This rather uncommon feature is also met in a high-pressure form of UO_3 (Siegel, Hoekstra & Sherry, 1966). Linkage between the chains proceeds *via* SO_4 or SeO_4 tetrahedra. Units of two pentagonal bipyramids linked by two tetrahedra are found, similar to those in $\text{UO}_2\text{SO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (van der Putten & Loopstra, 1974) and $\text{UO}_2\text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (Brandenburg & Loopstra, 1973).

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for $\beta\text{-UO}_2\text{SO}_4$ and $\alpha\text{-UO}_2\text{SeO}_4$

	$\beta\text{-UO}_2\text{SO}_4$	$\alpha\text{-UO}_2\text{SeO}_4$		$\beta\text{-UO}_2\text{SO}_4$	$\alpha\text{-UO}_2\text{SeO}_4$
U—O(1)	2.36 (2)	2.31 (3)	O(1)—U—O(2)	74.1 (6)	73.2 (6)
U—O(2)	2.30 (2)	2.33 (2)	O(2)—U—O(3)	75.9 (5)	73.6 (6)
U—O(3)	2.32 (2)	2.30 (2)	O(3)—U—O(4)	73.4 (5)	72.5 (7)
U—O(4)	2.36 (2)	2.39 (2)	O(4)—U—O(5)	68.0 (5)	71.8 (6)
U—O(5)	2.54 (2)	2.49 (2)	O(5)—U—O(1)	70.2 (5)	69.5 (6)
U—O(5)	1.80 (2)	1.79 (2)	O(5)—U—O(6)	176.1 (7)	175.2 (10)
U—O(6)	1.73 (1)	1.78 (2)			

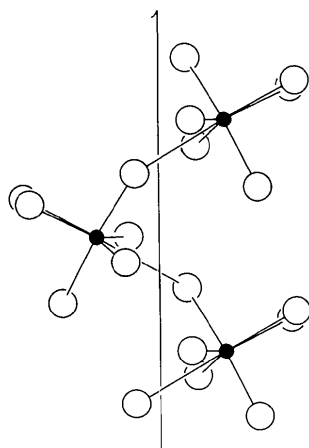


Fig. 3. Chain of U bipyramids along 2_1 axis in α - UO_2SeO_4 .

Fig. 2 shows that the main difference between β - UO_2SO_4 and α - UO_2SeO_4 is a slight change in the orientation of the bipyramids and tetrahedra. As we assume the structure of β - UO_2SeO_4 to be identical to that of β - UO_2SO_4 it appears that the phase transition between α - and β - UO_2SO_4 , although accompanied by a sizeable increase in cell volume, from a structural point

of view only involves minor rotation of the coordination polyhedra.

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Dimeric Dibromo(2,3-butanedione dioximato)copper(II)

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Abstract. $\text{C}_4\text{H}_8\text{N}_2\text{O}_2\text{CuBr}_2$, FW 339.5, triclinic $P\bar{1}$, $a = 7.759$ (1), $b = 8.594$ (1), $c = 8.273$ (1) Å, $\alpha = 71.56$ (1), $\beta = 69.08$ (1), $\gamma = 101.20$ (1)°, $V = 458.5$ (1) Å³, $Z = 2$, $D_c = 2.46$ g cm⁻³. There is one centrosymmetric dimer in the unit cell, bridged by two Br atoms. Chains are formed along x by hydrogen bridges (2.886 Å) between oxime O atoms of adjacent dimers. The coordination around each Cu is approximately square-pyramidal, the base formed by N and two strongly bonded Br atoms, the apex by a weakly bonded (2.883 Å) Br, belonging to the other Cu. The Cu–Cu distance is 3.599 Å. Atomic coordinates taken from the analogous chloro compound were refined by least squares to $R = 0.066$, based on 1696 observed reflections.

Introduction. Bridged Cu complexes have received much interest in recent years because of magnetic exchange between the paramagnetic Cu ions. [Reviews have been given by Hatfield (1974) and Hodgson (1975).] For a better understanding of the correlation between structural and magnetic properties it is desirable to have a series of compounds where only the bridging atoms are changed. In dealing with halide-bridged systems, there are a few pairs of compounds with amine or pyridine ligands and Cl or Br bridges (Table 2 and the references therein). Besides these ligands, halide-bridged complexes with dioximato ligands constitute another series of closely related compounds. Nevertheless, there is only one structure known, dimeric dichloro(2,3-butanedione dioximato)-