Uranyl Selenite and Uranyl Tellurite

By B. O. Loopstra and N. P. Brandenburg

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, *Amsterdam, The Netherlands*

Abstract. UO_2SeO_3, monoclinic, $P2_1/m$, $a = 5\cdot408$ (2), $b = 9\cdot278$ (1), $c = 4\cdot254_5$ (1) Å, $\beta = 93\cdot45$ (10)°, $V = 213\cdot1$ Å^3, $Z = 2$, $D_x = 6\cdot19$ g cm^{-3}. UO_2TeO_3, orthorhombic, $Pbcm$, $a = 5\cdot363$ (3), $b = 10\cdot161$ (4), $c = 7\cdot862$ (3) Å, $Z = 4$, $D_x = 6\cdot91$, $D_m = 6\cdot91$ (4) g cm^{-3}. The structure of uranyl selenite was solved from neutron powder data; that of uranyl tellurite was redetermined from Mo $K\alpha$ single-crystal data. Both structures are identical in a topological sense, but the coordination polyhedra of the heavy atoms are dissimilar.

Introduction. Polycrystalline UO_2SeO_3 was obtained during an investigation of uranyl selenates and selenites (Brandenburg & Cordfunke, 1978). Its structure was determined to obtain a better understanding of the thermochemical measurements of both this compound and uranyl tellurite.

A sample was prepared by heating a mixture of amorphous UO_3 with a slight excess of SeO_2 in a sealed and evacuated tube overnight at 360°C. After grinding in a dry box the product was again given the same treatment. Excess SeO_2 was removed by sublimation into the cooled empty part of the sample capsule. Analysis gave U 60·22% (59·96% calculated), Se 19·6% (19·89% calculated). The sample was of moderate crystallinity. X-ray powder pattern lines (Cu $K\alpha$, Guinier camera) were indexed with the computer program of Visser (1969). Errors in the cell constants quoted above represent the spread between various samples. In addition to the film data, step-scanned Cu $K\alpha$ X-ray diffractometer data were obtained. Neutron powder data were collected at the Petten HFR with slits $\alpha_1 = \alpha_3 = 10'$ in the range $0 < (\sin\theta)/\lambda < 0\cdot36$ Å^{-1}. The sample was contained in a thin-walled vanadium can, $\varnothing = 10$ mm. Neutrons with $\lambda = 2\cdot571$ Å were used.

Space group $P2_1$ or $P2_1/m$ was indicated by the systematic absences $0k0$ with $k = 2n + 1$. All X-ray lines with $k = 2n$ were found to be systematically stronger than those with $k = 2n + 1$. From this it follows that the U atoms must be at or close to the screw axis. A 35-term Patterson function was computed from the X-ray diffractometer data, separated into single reflections as far as possible. From this the

Se atom was found to be at $0\cdot66$, $0\cdot25$, $0\cdot37$ relative to the U atom. No further use was made of the X-ray data. The rest of the structure determination and refinement was based on the neutron data. Least-squares refinement with Rietveld's (1969) profile fitting program was attempted in $P2_1$ starting from a model based on seven-coordination of the U atom by O atoms. As this was unsuccessful the selenite O atoms were introduced in a refinement in which constraints maintained the known selenite dimensions. It then became clear that the space group is $P2_1/m$ with U at a centre of symmetry and hence Se in the mirror plane. The U atom is surrounded by eight O atoms at the corners of a hexagonal bipyramid. Final unconstrained refinement led to the coordinates of Table 1. The final R as defined by Rietveld (1969) is $0\cdot099$. Table 2 presents the main bond distances and angles. In Fig. 1 the observed and calculated pattern is shown. It is seen that the 002 peak at $2\theta = 74\cdot3°$ is poorly represented by the calculation. This is mainly due to an anomalous peak width in the observed pattern. In Fig. 2 the structure is depicted in projection along a.

In Table 3 the coordinates of UO_2TeO_3 as determined by Meunier & Galy (1973) are given (after transformation by $0,-1,0,0$; $1,0,0,0$; $0,0,1,\frac{1}{4}$). As also shown in Table 3, the atoms are found to be almost at the positions required by space group $Pbcm$. From the

Table 1. *Coordinates and thermal parameters for* UO_2SeO_3

	x	y	z	B (Å^2)
U	0	0	0	1·4 (3)
Se	0·692 (2)	$\frac{1}{4}$	0·400 (2)	0·9 (3)
O(1)	0·769 (2)	$\frac{1}{4}$	0·022 (3)	0·4 (4)
O(2)	0·886 (2)	0·107 (1)	0·501 (2)	2·3 (3)
O(3)	0·285 (2)	0·083 (1)	0·025 (2)	2·0 (3)

Table 2. *Selected bond lengths and angles in* UO_2SeO_3

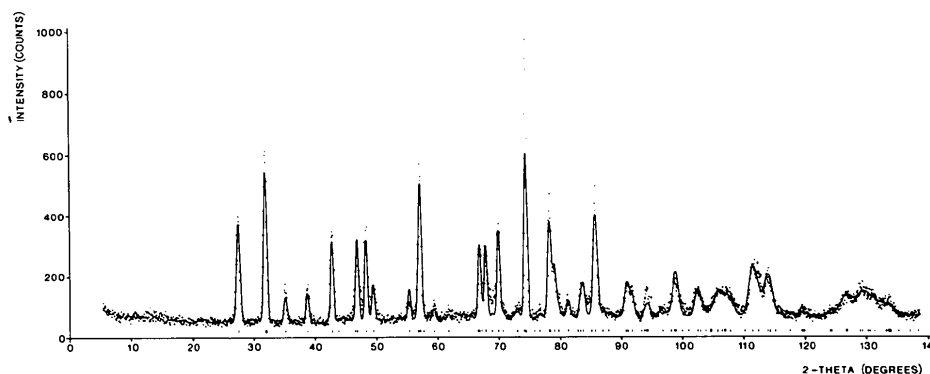|			
U–O(3)	1·72 (1) Å	O(1)–U–O(3)	91·6 (4)°
U–O(2)	2·39 (6)	O(2)–U–O(3)	92·1 (4)
U–O(2)	2·46 (5)	O(2)–U–O(3)	92·9 (4)
U–O(1)	2·64 (1)		
Se–O(1)	1·69 (4)	O(1)–Se–O(2)	93·2 (6)
Se–O(2)	1·73 (3)	O(2)–Se–O(2)	100·2 (7)

Fig. 1. Observed and calculated neutron powder pattern of UO_2SeO_3. Full line: calculated profile; dots: measurements.

Table 3. Comparison of space groups $Pbc2_1$ and $Pbcm$ for UO_2TeO_3

Under $Pbc2_1$, coordinates and e.s.d.'s are listed as obtained from those of Meunier & Galy (1973). Slight shifts suffice to introduce a centre of symmetry, as shown under $Pbcm$.

| | | $Pbc2_1$ | | | | $Pbcm$ | |
	x	y	z			x	y	z
U	0·9698 (2)	0·0148 (1)	0·250 (–)	U	4(d)	0·9698	0·0148	0·250
Te	0·6338 (4)	0·250 (2)	0·497 (2)	Te	4(c)	0·6338	0·250	0·500
O(1)	0·730 (5)	0·214 (3)	0·224 (4)	O(1)	4(d)	0·730	0·214	0·250
O(2)	0·839 (6)	0·103 (4)	0·534 (6)	O(2)	8(e)	0·860	0·106	0·526
O(3)	0·880 (8)	0·108 (5)	0·983 (7)					
O(4)	0·241 (6)	0·115 (3)	0·277 (4)	O(3)	4(d)	0·241	0·115	0·250
O(5)	0·694 (6)	0·910 (3)	0·281 (4)	O(4)	4(d)	0·694	0·910	0·250

Table 4. Coordinates and thermal parameters for UO_2TeO_3

	x	y	z	$B(Å^2)$
U	0·9698 (2)	0·0149 (1)	0·250 (–)	0·71 (3)
Te	0·6340 (4)	0·250 (–)	0·500 (–)	0·67 (4)
O(1)	0·732 (7)	0·214 (3)	0·250 (–)	2·6 (7)
O(2)	0·857 (4)	0·105 (2)	0·527 (3)	1·5 (4)
O(3)	0·244 (7)	0·115 (3)	0·250 (–)	2·2 (7)
O(4)	0·691 (8)	0·913 (4)	0·250 (–)	3·3 (8)

Table 5. Selected bond lengths and angles in UO_2TeO_3

U–O(3)	1·79 (4) Å	O(1)–U–O(3)	87·6 (14)°
U–O(4)	1·82 (4)	O(2)–U–O(3)	88·3 (9)
U–O(2)	2·33 (2)	O(2)–U–O(3)	89·5 (7)
U–O(1)	2·39 (3)	O(1)–U–O(4)	92·5 (16)
U–O(2)	2·44 (2)	O(2)–U–O(4)	91·7 (10)
U–O(1)	3·45 (4)	O(2)–U–O(4)	90·6 (8)
Te–O(2)	1·91 (2)	O(1)–Te–O(1)	150·5 (14)
Te–O(1)	2·07 (1)	O(1)–Te–O(2)	82·6 (12)
Te–O(4)	3·11 (3)	O(1)–Te–O(2)	79·0 (11)
Te–O(3)	3·18 (3)	O(2)–Te–O(2)	102·4 (9)

structure factor list deposited by Meunier & Galy (1973) the structure was redetermined in *Pbcm* with unit weights. For a refinement with isotropic temperature factors for all atoms R values of 0·060 (with 20 position parameters in $Pbc2_1$) and 0·062 (with 12 position parameters in *Pbcm*) were obtained. Aniso-
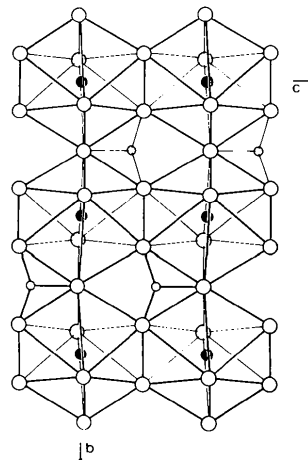
tropic temperature parameters for the U and Te atoms led to $R = 0·057_4$ and $0·057_8$ respectively. From this it is evident that space group *Pbcm* is to be preferred. Table 4 lists the final parameters and Table 5 the main bond lengths and angles obtained in the isotropic refinement. As the shifts are small the illustrations given by Meunier & Galy (1973) suffice to depict the structure.

Fig. 2. Structure of UO_2SeO_3 projected along a. Large circles: O; small circles: Se; filled circles: U. The hexagonal-bipyramidal O atom coordination around the U atoms has been drawn; the selenite ion is represented by Se—O bonds.

Discussion. Tables 1 and 4 illustrate the close similarity between UO_2SeO_3 and UO_2TeO_3 [O(3) in Table 1 corresponding to O(3) and O(4) in Table 4]. For the comparison the z parameters of Table 1 have to be changed to $0.250 + z/2$ because of the shift of origin and the doubling of c in the tellurite.

Although the two structures are topologically identical the two compounds are not isostructural. In UO_2SeO_3 the selenite ion has its usual trigonal-pyramidal shape; the U coordination is hexagonal bipyramidal (regarding the O atoms at 2.64 Å as part of the coordination polyhedron). This coordination is unusual for U^{VI}. In the tellurite the Te^{IV} coordination is close to the normal trigonal bipyramid with an empty site in the base plane (Zemann, 1971). As in α-TeO_2 (Lindqvist, 1968) the tellurite ion has a twofold axis. In the tellurite the U is coordinated by a pentagonal-bipyramidal arrangement of O atoms, which is rather more distorted than usual, apparently caused by O(1) at 3.45 Å.

UO_2SeO_3 is unstable in air and towards moisture, while UO_2TeO_3 occurs as a mineral. Both structures exhibit a large number of strong bonds in the yz layers, but the coherence in the x direction is small: two Se—O bonds of 3.06 Å per Se atom in the selenite and two Te—O bonds of 3.11 and two of 3.18 Å per Te atom in the tellurite. No other bonds exist up to the 3.5 Å limit calculated. If the valence of these bonds is calculated from the parameters given by Brown & Wu (1976) we find a value of 0.12 for the selenite and 0.12 and 0.11 for the tellurite bonds. These values indicate that the interlayer bond strength in the tellurite is twice that in the selenite. From the structures no other plausible explanation is found for the difference in stability between UO_2SeO_3 and UO_2TeO_3.

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Tetraaquabis(m-chlorobenzoato)nickel(II)

BY S. F. PAVKOVIC AND F. C. WILHELM

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626, USA

AND J. N. BROWN

Department of Chemistry, Illinois Institute of Technology, Chicao, Illinois 60616, USA

Abstract. $C_{14}H_{16}Cl_2O_8Ni$, $M_r = 441.89$, triclinic, $P\bar{1}$, $a = 6.273$ (1), $b = 10.021$ (1), $c = 13.696$ (2) Å, $\alpha = 90.14$ (1), $\beta = 95.74$ (1), $\gamma = 93.55$ (1)°, $Z = 2$, $D_c = 1.72$, $D_m = 1.71$ (2) g cm^{-3}; $R = 0.048$ for 2466 observed reflections. In this molecular compound the Ni atom is coordinated to O atoms in a pseudo-octahedral arrangement involving *trans* monodentate carboxylate anions.

Introduction. Initial precession photographs of a prismatic green crystal (0.3 mm) indicated a triclinic unit cell which structure analysis later showed to be $P\bar{1}$. The crystal was transferred to a Picker FACS-I fully automated diffractometer (b^* axis coincident with φ axis) and lattice constants were determined from 26 intense reflections by a least-squares fit to carefully measured $\pm 2\theta$ values ($60 < 2\theta < 78°$) for the Cu $K\alpha_1$ — $K\alpha_2$ doublet [λ(Cu $K\alpha_1$) = 1.54050 Å; λ(Cu $K\alpha_2$) = 1.54433 Å]. Intensity data were collected to a $2\theta_{max}$ of $125°$ with Ni-filtered Cu $K\alpha$ radiation (as the only available source) using a fixed $\theta/2\theta$ scan rate of $2°$ min^{-1}. A variable scan width of $2.3° + 0.4°$ tan θ with