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Synthesis and crystal structure determination, of $Pb_2[UO_2][TeO_3]_3$

F. Brandstätter*

Institut für Mineralogie und Kristallographie der Universität,
Dr.-Karl-Lueger-Ring 1, A-1010 Wien, Austria

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Abstract. Single crystals of $Pb_2[UO_2][TeO_3]_3$ were obtained by hydrothermal synthesis. The crystal data are: $a = 11.605(4)$, $b = 13.389(17)$, $c = 6.981(1)$ Å, $\beta = 91.23(3)°$, $Z = 4$, $D_x = 7.42(1)\,g \cdot cm^{-3}$. The structure was determined from X-ray intensities measured on a two-circle diffractometer and was refined for 2566 independent observed reflections to $R = 0.059$. It can be described as built up by $\{[UO_2][TeO_3]_3\}_n^{4n-}$ sheets parallel to (010) which are connected by lead atoms in irregular coordination.

Introduction

The attempts to synthesize hydrothermally the mineral moctezumite for which the formula $PbUTe_2O_8$ is given (Gaines, 1965), yielded small orange needles. As the lattice constant in the needle direction did agree reasonably well with the lattice constant b of moctezumite (Gaines, 1965), it was first thought that the phase was identical with this mineral. However, subsequent microprobe and X-ray diffraction work showed that the crystals obtained, although indeed a lead uranyl tellurite, were definitely different from moctezumite as described by Gaines (1965). As the compound described here could be easily synthesized in a wide mixture range of the starting materials, while moctezumite (fitting the description in the literature) was never obtained, it is expected, possibly to occur also in the mineral kingdom.

Experimental

The title compound was e.g., synthesized by hydrothermal treatment of a stoichiometric mixture of PbO, $UO_2(CH_3COO) \cdot 2\,H_2O$, and TeO_2 in a Teflon lined reactor. A temperature of about

* Present adress: Dr. F. Brandstätter, Naturhist. Museum Wien, Min.-Petr. Abteilung, Burgring 7, A-1014 Wien, Austria

230° was maintained for 60 h. After slow cooling the reaction product contained rosettes and single crystal needles, bright orange to brownish orange in color. A semi quantitative electron beam microanalysis (standards: synthetic schmitterite and natural linarite) gave an atomic ratio Pb : U : Te ≈ 2 : 1 : 3 which led to the probable formula $Pb_2UTe_3O_{11}$.

Lattice constants were derived from the least-squares fit of the reflecting positions of 24 reflections measured on a four-circle diffractometer (Philips PW 1100, measuring routine LAT, Mo$K\alpha$ radiation). The lattice parameters are: $a = 11.605(4)$, $b = 13.389(17)$, $c = 6.981(1)$ Å, $\beta = 91.23(3)°$. The space group was determined to be $P2_1/n$ due to the systematic absences $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$). With the probable assumption of a cell content of $4 \times Pb_2UTe_3O_{11}$, which in the course of the structure determination was verified one calculates $D_x = 7.42(1)\,g \cdot cm^{-3}$.

Structure determination and refinement

A well formed needle-like crystal measuring $15 \times 20 \times 400\,\mu m$ was mounted with [001] parallel to the main axis of a goniometer head. X-ray intensities were collected on an automatic two-circle diffractometer (Stoe Stadi-2, Mo$K\alpha$ radiation, graphite monochromator, ω-scan, $\sin\vartheta/\lambda \leq 0.7\,Å^{-1}$). All reflections within the $\sin\vartheta/\lambda$-sphere with the conditions $k \geq 0$, $l \geq 0$ were measured, giving data of 2921 intensities; of these 355 were below the observation limit [$|F_o| = 2.5\sigma(F_o)$]. The intensities were corrected for absorption (transmission factors ranged from 0.309 to 0.496) as well as Lorentz- and polarization effects.

As a trial to interpret a threedimensional Patterson synthesis failed, resort to direct methods (Multan, Main et al., 1974) was taken. An E-map showed six prominent maxima in the asymmetric unit. Three of them were much higher than the rest; they were interpreted as (Pb,U) atoms, while the three relatively lower ones were interpreted as Te atoms. A following least-squares refinement with the data with $\sin\vartheta/\lambda \leq 0.5\,Å^{-1}$, varying individual scale factors and isotropic temperature factors converged to a conventional $R = 0.12$. A subsequent difference Fourier synthesis revealed the positions of all the oxygen atoms. From crystal chemical reasons the distinction between Pb and U was now easily possible.

In the course of the full matrix least-squares refinement of all atoms with 2566 reflections [$|F_o| > 2.5\sigma(F_o)$] a conventional reliability index $R = 0.059$ was obtained; for all 2921 reflections $R = 0.076$. During the refinement 51 positional coordinates, 36 anisotropic temperature factor components (for U, Pb, Te), 11 isotropic temperature factors (for O), and 10 individual scale factors were varied. The scattering factors of the neutral atoms U, Pb, O, and Te as well as their anomalous dispersion terms were taken from the "International Tables of Crystallography" Vol. IV (1974). A final difference map showed only peaks with a peak height smaller than one fourth of the oxygen Fourier peak height with no indication of incorrectly placed or missing atoms. The final atomic coordinates and the thermal vibration parameters are given in Table 1. The calculated powder diagram based on this determination is given in Table 2.

Table 1. Atomic coordinates and thermal vibration parameters. Standard deviations (in units of the last digit) in brackets

Atom	x	y	z	B_{iso} ($Å^2$)
(a) Atomic coordinates and isotropic temperature factors				
U	0.25733(7)	0.72025(6)	0.89223(12)	0.45
Pb(1)	0.06306(8)	0.95061(8)	0.72689(15)	1.45
Pb(2)	0.43834(8)	0.00349(7)	0.74333(13)	1.02
Te(1)	0.41357(11)	0.76171(11)	0.43221(22)	0.67
Te(2)	0.75571(12)	0.98229(11)	0.78003(22)	0.81
Te(3)	0.07353(11)	0.74500(11)	0.40704(22)	0.57
O(1)	0.7661(14)	0.1591(14)	0.0102(28)	1.48(29)
O(2)	0.8250(14)	0.2207(13)	0.3833(26)	1.38(28)
O(3)	0.5948(12)	0.2137(11)	0.2983(22)	0.44(22)
O(4)	0.9403(13)	0.3216(12)	0.0859(24)	0.82(24)
O(5)	0.4475(13)	0.1077(12)	0.0245(25)	0.96(25)
O(6)	0.0451(13)	0.1285(12)	0.0332(24)	0.88(25)
O(7)	0.2518(13)	0.1511(12)	0.3166(24)	0.79(24)
O(8)	0.0516(12)	0.2002(11)	0.4623(23)	0.60(23)
O(9)	0.1301(11)	0.4635(10)	0.1308(21)	0.34(21)
O(10)	0.3790(15)	0.4766(14)	0.1421(28)	1.57(30)
O(11)	0.7289(12)	0.4010(12)	0.2271(23)	0.72(24)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
(b) Anisotropic temperature factors. T.F. $= \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + \cdots + 2B_{23}b^*c^*kl)]$ in [$Å^2$]						
U	0.33(3)	0.58(3)	0.43(3)	−0.00(2)	0.03(2)	0.00(3)
Pb(1)	1.12(3)	1.84(4)	1.39(4)	−0.25(3)	0.02(3)	0.46(3)
Pb(2)	1.01(3)	1.18(3)	0.86(3)	0.12(3)	0.01(3)	−0.06(3)
Te(1)	0.42(4)	0.93(5)	0.65(5)	−0.11(4)	0.02(4)	−0.13(5)
Te(2)	0.80(5)	0.84(5)	0.79(5)	0.04(4)	−0.01(5)	−0.12(5)
Te(3)	0.46(4)	0.49(5)	0.75(5)	−0.06(4)	−0.01(4)	0.00(5)

Discussion and description

Interatomic distances and bond angles are summarized in Table 3. A projection of the structure parallel [001] is shown in Figure 2.

The only uranium atom in the asymmetric unit forms an uranyl group with an angle (O)−U−(O) of 174° and an average U−O bond length of 1.80 Å. Five further equatorial oxygens have U−O bond distances between 2.24 and 2.43 Å (average 2.34 Å); the distances from their least-squares plane vary only from 0.01 to 0.09 Å. All seven oxygens around uranium form a flattened pentagonal bipyramidal coordination. Similar uraniumoxygen coordination polyhedra have been found in many other uranyl compounds (Pertlik, 1974; Rosenzweig and Ryan, 1977; Brandenburg and Loopstra,

Table 2. Theoretical powder diffractogram (Debye-Scherrer, Cu$K\alpha$-radiation) as calculated from determined structure

h	k	l	I	d (in Å)	h	k	l	I	d (in Å)
−1	0	1	10	6.038	0	5	2	7	2.224
1	0	1	5	5.925	−1	5	2	11	2.095
1	2	0	6	5.799	3	5	1	10	2.092
−1	1	1	10	5.504	5	2	1	5	2.080
2	2	0	22	4.384	−3	0	3	27	2.013
−2	2	1	5	3.740	3	0	3	25	1.975
1	3	1	21	3.565	6	0	0	23	1.934
2	3	0	7	3.537	3	6	0	13	1.933
0	0	2	15	3.490	0	6	2	7	1.880
−3	0	1	9	3.414	−3	6	1	9	1.858
0	1	2	46	3.377	2	7	1	7	1.755
3	0	1	7	3.352	−3	4	3	19	1.725
3	2	0	13	3.349	3	4	3	19	1.701
0	4	0	82	3.347	−6	1	2	7	1.693
−3	1	1	38	3.308	0	2	4	17	1.688
3	1	1	48	3.252	6	4	0	15	1.674
2	3	1	9	3.139	1	7	2	8	1.658
0	2	2	96	3.095	−6	2	2	10	1.654
−3	2	1	100	3.041	6	2	2	8	1.626
0	4	1	17	3.018	0	6	3	6	1.610
3	2	1	90	2.998	6	3	2	7	1.569
−2	1	2	6	2.945	−4	7	1	5	1.561
4	0	0	6	2.901					
0	3	2	24	2.749					
−3	3	1	22	2.712					
2	2	2	6	2.709					
3	3	1	10	2.681					
1	5	0	7	2.609					
0	5	1	5	2.500					
1	5	1	5	2.440					
0	4	2	5	2.416					
−5	0	1	7	2.216					

1978; Loopstra and Brandenburg, 1978; Mereiter, 1979). The average bond lengths of this work are quite close to the values 1.81 Å (uranyl) and 2.35 Å (equatorial) found in the minerals kasolite (Rosenzweig and Ryan, 1977) and sklodowskite (Rosenzweig and Ryan, 1977).

The two crystallographic different lead atoms possess irregular oxygen coordinations. Pb(1) is bound to eight O atoms, Pb(2) to seven O neighbours. The oxygens around Pb(1) and Pb(2) show a strong tendency to an one-sided coordination due to the presence of a lone pair of 6 s-electrons (e.g. Sahl, 1972). Some recently determined Pb(II) compounds with similar Pb−O distances are $PbK_2(PO_3)_4$ (Brunel-Läugt and Guitel, 1977); $Pb_3(P_3O_9)_2 \cdot H_2O$

Table 3. Interatomic distances (Å) and bond angles (°). Standard deviations (in units of last figure) in brackets

		O–U–O angle
(a) Coordination of uranium		
U–O(1) = 1.776(18)	O(1) –O(11)	174.4(7)
–O(11) = 1.832(16)	–O(2) = 2.803(26)	86.8(7)
–O(7) = 2.238(17)	–O(3) = 2.950(23)	89.7(7)
–O(2) = 2.271(18)	–O(7) = 2.881(24)	91.0(7)
–O(3) = 2.366(14)	–O(4) = 3.009(23)	92.0(7)
–O(4) = 2.369(15)	–O(8) = 3.133(22)	94.9(7)
–O(8) = 2.433(15)	O(11)–O(7) = 2.967(23)	93.0(7)
	–O(2) = 2.864(23)	87.8(7)
	–O(3) = 2.999(21)	90.3(6)
	–O(4) = 2.867(21)	85.1(6)
	–O(8) = 3.503(21)	90.3(6)
	O(7) –O(4) = 2.877(22)	77.2(6)
	O(4) –O(2) = 2.836(24)	75.3(6)
	O(2) –O(3) = 2.727(22)	72.0(6)
	O(3) –O(8) = 2.652(22)[a]	67.1(5)
	O(8) –O(7) = 2.639(21)	68.6(6)
(b) Coordination of lead atoms		
Pb(1)–O(6) = 2.365(16)	Pb(2)–O(5) = 2.408(17)	
–O(10) = 2.410(18)	–O(9) = 2.417(13)	
–O(10) = 2.699(19)	–O(5) = 2.551(16)	
–O(8) = 2.742(15)	–O(4) = 2.587(16)	
–O(2) = 2.754(17)	–O(11) = 2.747(15)	
–O(11) = 2.767(15)	–O(9) = 2.766(15)	
–O(1) = 3.050(18)	–O(3) = 2.946(15)	
–O(6) = 3.210(16)		
		O–Te–O angle
(c) Coordination of tellurium atoms		
Te(1)–O(6) = 1.862(16)	O(6) –O(4) = 2.885(22)	100.8(7)
–O(4) = 1.882(15)	O(6) –O(3) = 2.744(22)	93.2(7)
–O(3) = 1.914(15)	O(4) –O(3) = 2.760(22)	93.3(7)
–O(9) = 2.782(14)		
–O(8) = 2.911(16)		
–O(7) = 2.958(16)		
–O(2) = 3.088(17)		
Te(2)–O(10) = 1.827(18)	O(10)–O(7) = 2.805(24)	97.2(7)
–O(7) = 1.911(16)	O(10)–O(9) = 2.893(22)	101.2(7)
–O(9) = 1.916(14)	O(7) –O(9) = 2.881(21)	97.7(6)
–O(1) = 2.862(18)		
–O(5) = 3.002(16)		
–O(6) = 3.019(16)		

[a] Common edge between UO_7 and $Te(3)O_4$

Table 3. Continued

Te(3)–O(8) = 1.881(15)	O(8) –O(2) = 2.690(22)	90.3(7)
–O(2) = 1.914(18)	O(8) –O(5) = 2.879(22)	98.6(7)
–O(5) = 1.917(16)	O(2) –O(5) = 2.865(24)	96.8(7)
–O(3) = 2.434(14)	O(8) –O(3) = 2.652(11)[a]	74.6(6)
–O(7) = 2.874(16)		
–O(10) = 3.169(19)		

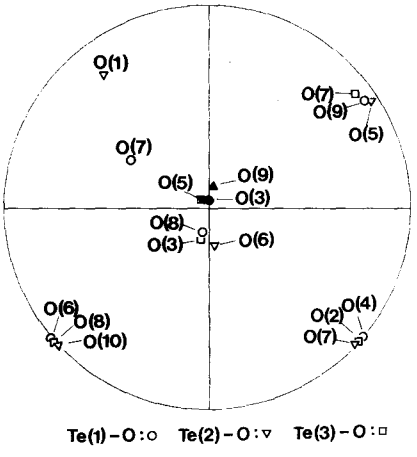

Fig. 1.
Stereographic projection of the Te(IV)–O bond directions in $Pb_2[UO_2][TeO_3]_3$ as proposed by Zemann (1971)

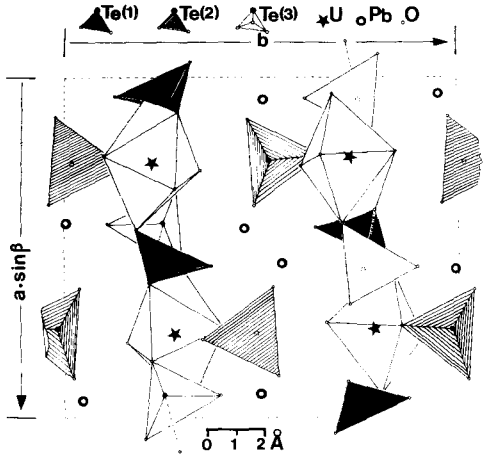

Fig. 2.
$Pb_2[UO_2][TeO_3]_3$. Projection parallel [001]

(Brunel-Läugt et al., 1977); kasolite, $Pb(UO_2)(SiO_4) \cdot H_2O$ (Rosenzweig and Ryan, 1977); and $PbTi_3O_7$ (Kato et al., 1974).

The asymmetric unit contains three tellurium atoms which have the one-sided coordination geometry as typical for Te(IV). For surveys of the stereochemistry of Te(IV) the reader is referred to Bayer (1969), Lindqvist (1973), Zemann (1968, 1971, 1974), and Galy et al. (1975). The bond directions around the three Te atoms are given in Figure 1 in stereographic projection following the orientation convention of Zemann (1971). It is seen that their mutual orientation corresponds to common experience. Te(1) and Te(2) have a pretty clear pyramidal coordination, while the surrounding of Te(3) can also be described as (3 + 1)-coordinated.

The atomic arrangement can be described as being built of sheets parallel to (010) which are composed of the UO_7 polyhedra and the tellurium-oxygen pyramids. Te(1) is connected to two UO_7 polyhedra (via two oxygens), Te(2) to only one UO_7 polyhedron (via one oxygen), and Te(3) to two UO_7 polyhedra (via two oxygens if considered as 3-coordinated, via three oxygens if considered to be 4-coordinated – in the last case, $Te(3)O_4$ and UO_7 have a common edge). For details see Figure 3. The sheet-like $\{[UO_2][TeO_3]_3\}_n^{4n-}$ units are held together by the in-between lead atoms. Each two Pb atoms related by a center of symmetry yield the shortest Pb–Pb distances: Pb(1)–Pb(1) = 3.71 Å, Pb(2)–Pb(2) = 3.72 Å. With the coordinations given in Table 3 each Pb polyhedron shares two edges with two neighbouring Pb polyhedra leading to chains parallel to [001]. These chains help to explain the morphological elongation of the crystals parallel to [001].

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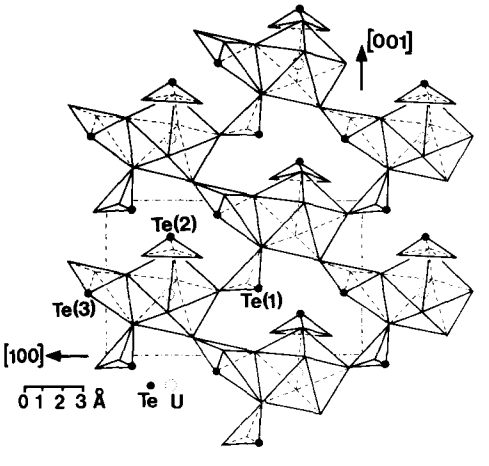

Fig. 3. $\{[UO_2][TeO_3]_3\}_n^{4n-}$ – "sheet". Projection parallel [010]

G. Sheldrick (SHELX-76) and C. T. Prewitt (SFLS-5) as adopted by Dr. R. Fischer and Dr. K. Mereiter, respectively, were used. MULTAN (Main et al.) was adopted by Dr. H. Völlenkle. Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" (Project Nr. 3461) is gratefully acknowledged.

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