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Single-Crystal Structure of Lead Uranate(VI)

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Abstract. $PbUO_4$, $M_r = 509.2$, orthorhombic, Pbcm, $a = 5.536$ (1), $b = 7.968$ (2), $c = 8.212$ (3) Å, $Z = 4$, $V = 362.24$ Å^3, $D_x = 9.34$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu(Mo\,K\alpha) = 889.1$ cm^{-1}, $F(000) = 824$, $T = 298$ K, $R = 0.048$ for 530 unique observed reflections having $I \geq 2\sigma(I)$. As in the case of $BaUO_4$, $PbUO_4$ forms a layered structure of $(UO_2O_4)^{2-}_\infty$ sheets, with the divalent cations in approximate seven coordination sandwiched between the layers. The uranyl groups are in typical octahedral coordination.

Introduction. Several previous studies have been performed to determine the structures of uranates in general (e.g. Gebert, Hoekstra, Reis & Peterson, 1978; Kovba, Polunina, Simanov & Ippolitova, 1961; Peters, 1967) and lead uranate in particular (Frondel & Barnes, 1958; Sterns, 1967). Although until now no single-crystal diffraction study has been performed that yielded atomic positions, X-ray powder diffraction has shown the structure of $PbUO_4$ to be isomorphous with $BaUO_4$ (Frondel & Barnes, 1958; Reis, Hoekstra, Gebert & Peterson, 1976; Samson & Sillén, 1947). The present structure confirms the powder studies and has yielded precise atomic positional parameters for $PbUO_4$.

Experimental. Lead uranate ($PbUO_4$) was prepared from a melt by adding 2.5 g of PbClF to 0.25 g $U(MoO_4)_2$ (Cremers, Eller, Penneman & Herrick, 1983) and heating overnight at 823 K. Orange crystals were recovered from the solidified melt. The crystals are tabular on {100}, and bounded by prominent {011} and minor {001} and {010} faces. Good cleavage is present perpendicular to each of the crystallographic axes. The refractive indices exceed 1.700, and the optical orientation is $a = Z$, $b = Y$, $c = X$ with no distinctive pleochroism. The crystals are biaxial positive with a large angle and strong $r > v$ axial dispersion.

A crystal (0.028 × 0.090 × 0.082 mm) in the form of a square tablet was chosen for X-ray diffraction and mounted perpendicular to the {100} face. The data set was collected by θ–2θ scans ($2\theta_{max} = 70°$) on a Picker automated diffractometer using Mo $K\alpha$ radiation and a graphite monochromator. Precession photographs were used to verify the Laue symmetry and to obtain initial cell constants. The least-squares-refined cell dimensions based on twelve diffractometer-centered reflections ($40 \leq 2\theta \leq 53°$) are $a = 5.536$ (1), $b = 7.968$ (2) and $c = 8.212$ (3) Å. The space group as determined from systematically absent reflections was $Pbc2_1$ or Pbcm, and Pbcm was chosen on the basis of the subsequent successful refinement in the centrosymmetric cell. Reflections in a hemisphere with Miller indices $h\,0$–8, $k\,0\pm12$, and $l\,0\pm13$ were collected to yield 846 symmetry-independent reflections. Two standard reflections monitored approximately every 2 h. Analytical absorption corrections based on the indexed faces (max. transmission = 0.127, min. = 0.016) and corrections for Lorentz–polarization factors were performed. Equivalent reflections were averaged, yielding 530 reflections with $I \geq 2\sigma(I)$ and an R factor on F of 6%. The structure was solved using standard Patterson methods and refined by full-matrix least squares employing the Los Alamos Crystal Structure Codes

(Larson, 1977). The function minimized was $w(|F_o| - |F_c|)^2$ and weights were determined by $w = [2F_o/\sigma F_o^2]^2$. The calculations converged giving final conventional residuals of $R = 0.048$ and $wR = 0.064$ for the 530 reflections above background, with a maximum shift/standard deviation $= 0.005$. Anisotropic thermal parameters and positional parameters for the five unique atoms (with appropriate symmetry constraints) plus a scale factor and extinction parameter [final value 4.74×10^{-5} as defined in Larson (1970)] were refined, totalling 34 parameters. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). In a final difference synthesis, the largest feature was a peak near U, with height about one-third that of an O atom.
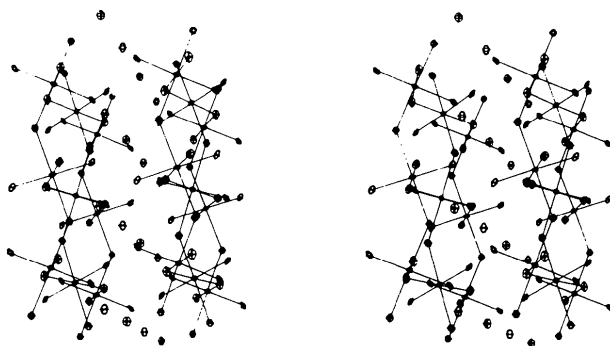

Fig. 1. Stereoscopic view of the unit cell of PbUO₄.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for PbUO₄*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$, where $\beta_{ij} = 2\pi^2 U_{ij}a_i^*a_j^*$.

	Site symmetry	x	y	z	B_{eq} or $B(\text{Å}^2)$
U	$\bar{1}$	0	0	0	0.466
Pb	m	0.4954 (5)	0.2022 (1)	$\frac{1}{4}$	1.182
O(1)	1	0.2915 (33)	0.9190 (19)	0.0765 (17)	0.923
O(2)	2	0.1587 (49)	$\frac{1}{4}$	0	0.954
O(3)	m	0.8701 (50)	0.0374 (31)	$\frac{1}{4}$	0.988

Table 2. *Interatomic distances (Å) and angles (°)*

U–O(1)	1.848 (18)	(×2)	U–U	3.984 (1)	(×2)
U–O(2)	2.177 (11)	(×2)	U–U	4.106 (1)	(×2)
U–O(3)	2.195 (9)	(×2)	U–Pb	3.786 (2)	(×2)
Pb–O(1)	2.897 (16)	(×2)	U–Pb	3.822 (2)	(×2)
Pb–O(1)	2.531 (15)	(×2)	Pb–Pb	3.984 (1)	(×2)
Pb–O(2)	2.799 (18)	(×2)	Pb–Pb	4.176 (1)	(×2)
Pb–O(3)	2.455 (26)				
U–O(1)–Pb	103.6 (6)		C(2)–U–O(3)	89.6 (7)	
U–O(1)–Pb	146.8 (8)		O(2)–U–O(3)	90.4 (7)	
U–O(2)–U	132.4 (13)		O(1)–Pb–O(1)	58.9 (3)	
U–O(2)–Pb	113.2 (3)		O(1)–Pb–O(1)	115.9 (5)	
U–O(2)–Pb	98.3 (3)		O(1)–Pb–O(1)	171.9 (7)	
U–O(3)–U	138.5 (13)		O(1)–Pb–O(2)	59.0 (3)	
U–O(3)–Pb	110.5 (6)		O(1)–Pb–O(2)	102.0 (5)	
O(1)–U–O(1)	180.0		O(1)–Pb–O(3)	85.0 (6)	
O(2)–U–O(2)	180.0		C(1)–Pb–O(1)	68.5 (4)	
O(3)–U–O(3)	180.0		O(1)–Pb–O(2)	78.7 (5)	
O(1)–U–O(2)	88.1 (8)		O(1)–Pb–O(2)	129.1 (4)	
O(1)–U–O(2)	91.9 (8)		O(1)–Pb–O(3)	88.4 (7)	
O(1)–U–O(3)	89.1 (8)		O(2)–Pb–O(2)	94.4 (8)	
O(1)–U–O(3)	90.9 (8)		O(2)–Pb–O(3)	129.5 (4)	

Discussion. A stereoscopic view of the PbUO₄ structure is depicted in Fig. 1. The fractional coordinates with their standard deviations and equivalent isotropic thermal parameters are listed in Table 1. Selected distances and angles are given in Table 2.*

Cell constants from the present study are in agreement with the earlier powder-derived unit cell for PbUO₄ (Frondel & Barnes, 1958) and the structure refinement confirms that PbUO₄ is isomorphous with BaUO₄ (Reis *et al.*, 1976). Fig. 1 shows the distinct layer structure of the compound with Pb ions sandwiched between infinite $(UO_2O_4)^{2-}$ sheets. The structure contains uranyl groups in typical octahedral coordination [$U-O_{ax} = 1.85$, $U-O_{eq} = 2.19$ Å (mean)] and lead in approximate seven coordination (Pb–O = 2.46–2.90 Å). Additional weak Pb–O contacts are seen at 3.1, 3.3 and 3.7 Å. The average of the seven shortest Pb–O distances is 2.70 Å whereas the mean Ba–O distance in BaUO₄ is 2.77 Å. Thus the Pb–O contacts are uniformly shorter than the Ba–O contacts, leading to a slightly smaller unit cell for PbUO₄ owing to the smaller ionic radius Pb^{II} compared with Ba^{II} (Shannon, 1976).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43117 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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