Refinement of the Structure of Trilead(II) Uranate(VI) from Neutron Powder Diffraction Data

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Abstract. Pb_3UO_6, $M_r = 955\cdot6$, orthorhombic, *Pnam*, $a = 13\cdot719$ (1), $b = 12\cdot351$ (1), $c = 8\cdot213$ (1) Å, $V = 1391\cdot7$ (4) Å^3, $Z = 8$, $D_x = 9\cdot120$ g cm^{-3}, high-resolution neutron powder diffraction data ($\lambda = 1\cdot500$ Å, $T = 295$ K), collected from 8·04 to 95·79° in 2θ with a 0·05° step size; final weighted pattern R factor was 0·046, compared to the 'expected' value of 0·037 (conventional R factor based on integrated intensities $= 0\cdot015$). The refinement confirmed the oxygen positions and hence the irregular oxygen coordination of lead found in the X-ray study of Pb_3UO_6 [Sterns (1967). *Acta Cryst.* **23**, 264–272].

Introduction. The structure analysis of Pb_3UO_6 (Sterns, 1967), from visually estimated photographic X-ray data, revealed a unique structure, containing corner-linked UO_6 octahedra, unlike the structures of the other known tri-orthouranates M_3UO_6 which are of a distorted cryolite type (Rietveld, 1966). The oxygen environment of lead in Pb_3UO_6 is so irregular that there was some doubt about the correctness of the oxygen positions determined in the X-ray study. This prompted us to check the structure using neutron powder diffraction data.

Experimental. Single-phase polycrystalline Pb_3UO_6 was prepared from PbO and $PbUO_4$ as described previously (Sterns, 1967). Neutron powder profile recorded at 295 K on the high-resolution eight-counter neutron powder diffractometer (HRPD) at the Australian Atomic Energy Commission HIFAR reactor, Lucas Heights (Howard, Ball, Davis & Elcombe, 1983), 2θ 8·04–95·79° in steps of 0·05°; sample contained in vanadium can *ca* 12 mm diameter, 50 mm high; neutron wavelength 1·500 Å, obtained by reflection

from 335 planes of 'squashed' Ge crystal monochromator with take-off angle 120°; monochromator mosaic spread *ca* 0·2°; 770 Bragg reflections in recorded range. Data analyzed with the Rietveld technique (Rietveld, 1969) using a version of the program of Wiles & Young (1981), significantly modified by Howard (1982) and Hill (1985). Starting with the atomic parameters from the X-ray structure determination, refinement of positional parameters, individual isotropic thermal parameters, overall scale factor, unit-cell constants, three background parameters, asymmetry parameter and diffractometer zero point gave the final discrepancy factors listed in Table 1. The calculated and observed neutron powder patterns are shown in Fig. 1.*

Discussion. The final refined atomic parameters are listed in Table 1 and metal–oxygen distances shorter than 3·5 Å, together with the corresponding distances from the X-ray study, are given in Table 2. The largest differences between the two sets of distances, 0·12 Å, are of the order of the estimated maximum error (0·1 Å) of metal–oxygen distances derived from the X-ray data. The structure, described in some detail in the earlier publication (Sterns, 1967), was thus confirmed quite satisfactorily by the refinement. Fig. 2 shows the packing of atoms in Pb_3UO_6, with metal–oxygen distances less than 3·0 Å shown as 'bonds'.

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* Numerical data corresponding to the primary diffraction record and a table of bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42987 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The octahedral coordination of uranium is as expected for U^{6+} in uranate structures. The bonds to the two oxygen atoms shared by two uranium atoms are rather shorter (by more than 10σ) than the other four U—O bonds. The coordination polyhedra of lead atoms Pb(1), Pb(2) and Pb(5) are shown in Fig. 3. The coordination of Pb(3) and Pb(4) is similar to that of Pb(2) and is not shown. The asymmetric oxygen environment of all lead atoms in the structure, with the shorter Pb—O bonds all to one side, is in accord with the presence of stereochemically active $6s^2$ lone electron pairs. The irregular eightfold coordination of Pb(1) is reminiscent of the lead coordination reported for $Pb_3GeGa_{10}O_{20}$ (Cadee, Verschoor & IJdo, 1983). The coordination polyhedra of Pb(2), Pb(3) and Pb(4) can be described approximately as pentagonal pyramids, or possibly as pentagonal bipyramids with the lone pair at one apex. The equatorial oxygen atoms are displaced towards the apical oxygens, i.e. away from the lone

Table 2. *Metal—oxygen distances* (Å) *for* Pb_3UO_6 *calculated from* (a) *neutron data and* (b) *X-ray data* (*Sterns,* 1967)

	(a)	(b)		(a)	(b)
U—O(1)	2·167 (9)	2·15	Pb(3)—O(4)	2·276 (16)	2·31
U—O(2)	2·214 (9)	2·19	Pb(3)—O(5)	2·434 (10) 2×	2·45
U—O(5)	2·040 (11)	2·03	Pb(3)—O(2)	2·611 (15)	2·62
U—O(6)	2·060 (11)	2·05	Pb(3)—O(8)	2·869 (9) 2×	2·88
U—O(7)	2·049 (11)	2·04	Pb(4)—O(3)	2·208 (13)	2·18
U—O(8)	1·991 (11)	1·90	Pb(4)—O(8)	2·496 (10) 2×	2·57
Pb(1)—O(7)	2·343 (11) 2×	2·34	Pb(4)—O(5)	2·682 (9) 2×	2·62
Pb(1)—O(3)	2·453 (14)	2·53	Pb(4)—O(1)	2·576 (14)	2·64
Pb(1)—O(8)	2·716 (10) 2×	2·75	Pb(5)—O(3)	2·260 (8)	2·24
Pb(1)—O(1)	3·149 (15)	3·14	Pb(5)—O(4)	2·359 (10)	2·36
Pb(1)—O(7')	3·210 (11) 2×	3·18	Pb(5)—O(7)	2·430 (10)	2·38
Pb(2)—O(4)	2·371 (15)	2·30	Pb(5)—O(6)	2·539 (10)	2·54
Pb(2)—O(6)	2·369 (11) 2×	2·40	Pb(5)—O(5)	2·805 (11)	2·91
Pb(2)—O(2)	2·621 (17)	2·72	Pb(5)—O(5')	3·467 (11)	3·35
Pb(2)—O(6')	2·817 (10) 2×	2·76			

Table 1. *Results of Rietveld refinement of the structure of* Pb_3UO_6

	x	y	z	B(Å²)
U	0·4146 (5)	0·2605 (6)	0·0016 (10)	0·6 (1)
Pb(1)	0·0311 (6)	0·0277 (6)	¼	0·5 (2)
Pb(2)	0·0057 (6)	0·5145 (8)	¼	1·3 (2)
Pb(3)	0·3521 (5)	0·7310 (7)	¼	0·6 (2)
Pb(4)	0·1832 (5)	0·2629 (6)	¼	0·5 (2)
Pb(5)	0·2683 (4)	0·0036 (5)	0·0300 (5)	0·5 (1)
O(1)	0·3692 (9)	0·2915 (10)	¼	0·4 (3)
O(2)	0·0380 (10)	0·7237 (11)	¼	1·5 (3)
O(3)	0·2022 (8)	0·0854 (9)	¼	0·3 (3)
O(4)	0·3449 (9)	0·9151 (11)	¼	1·2 (3)
O(5)	0·2291 (6)	0·7265 (7)	0·0366 (10)	1·4 (2)
O(6)	0·4321 (6)	0·0982 (7)	0·0516 (11)	1·2 (2)
O(7)	0·1085 (7)	0·9202 (7)	0·0537 (12)	1·8 (2)
O(8)	0·0523 (6)	0·2050 (7)	0·0577 (10)	1·8 (2)

Scattering lengths used: U 8·42, Pb 9·40, O 5·80 fm
Function minimized: $R = \Sigma_i w_i [y_i(\text{obs.}) - y_i(\text{calc.})]^2$

$R_p = \Sigma |y(\text{obs.}) - y(\text{calc.})| / \Sigma y(\text{obs.}) = 0\cdot040$: 'pattern R factor'
$R_w = \{\Sigma w[y(\text{obs.}) - y(\text{calc.})]^2 / \Sigma wy^2(\text{obs.})\}^{1/2} = 0\cdot046$: 'weighted pattern R factor'
$R_B = |\Sigma I(\text{obs.}) - I(\text{calc.})| \Sigma I(\text{obs.}) = 0\cdot015$: 'Bragg R factor'
$R_e = [(N-P)/\Sigma wy^2(\text{obs.})]^{1/2} = 0\cdot037$: 'expected weighted pattern R factor'

where y(obs.) and y(calc.) are the observed and calculated intensities, I(obs.) and I(calc.) the observed and calculated integrated intensities, N the number of statistically independent observations, P the number of parameters refined and $w = 1/\sigma^2$ the weights associated with y(obs.).
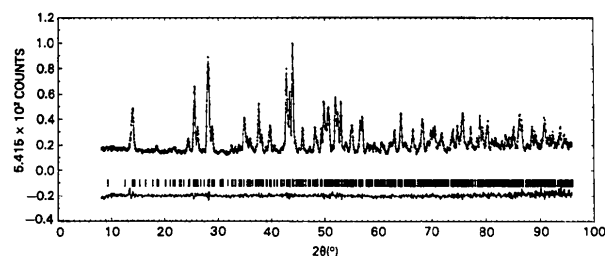

Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of Pb_3UO_6. The difference (observed − calculated) profile is shown below the pattern.
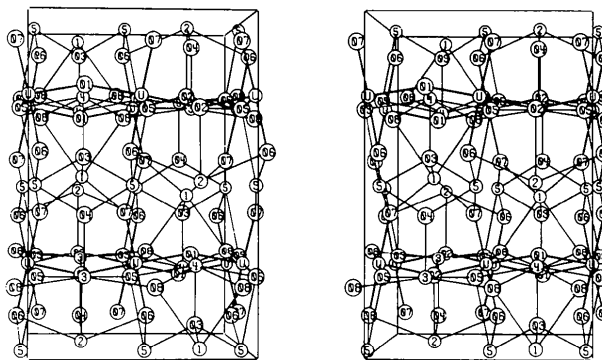

Fig. 2. Stereoscopic view of atomic packing in Pb_3UO_6 (b axis vertical, c axis horizontal) (*ORTEP*, Johnson, 1965). Metal–oxygen separations of less than 3·0 Å are shown as 'bonds'. Lead atoms are designated by numbers only.
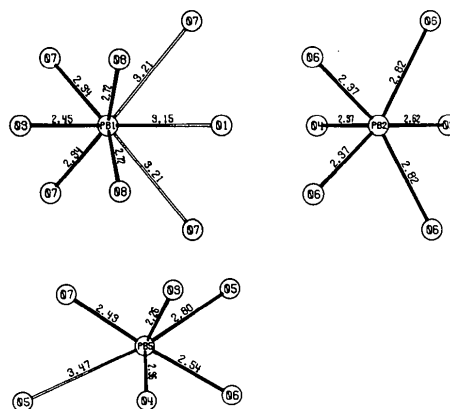

Fig. 3. Coordination polyhedra of lead atoms Pb(1), Pb(2) and Pb(5). Lead–oxygen distances of less than 3·0 Å are shown as dark sticks.

pairs. The only lead atoms not situated on mirror planes, Pb(5), exhibit an oxygen coordination (five- or sixfold, depending on whether oxygen atoms at 3·5 Å are considered to be in the coordination sphere) which is too irregular to be described in terms of any conventional polyhedron.

The pentagonal pyramids around Pb(3) and Pb(4) share edges with the UO_6 octahedra and with each other, resulting in layers $(PbUO_6)_\infty$ perpendicular to **b**. The remaining three lead atoms, each with a different oxygen environment, are distributed between the layers, in such a way that the structure exhibits rather large 'voids' towards which the lone pairs from all five types of lead atoms appear to be directed (*cf.* Fig. 2).

We thank a referee for pointing out that the formula $2PbO.PbUO_4$ would be preferable to Pb_3UO_6, in line with the terminology used for solid-solution phases formed by PbO with compounds such as $PbSO_4$, described by the general formula $nPbO.PbSO_4$. This is certainly in accord with the mode of formation of Pb_3UO_6 and of the other discrete phase in the $PbO–PbUO_4$ system, $Pb_{11}U_5O_{26}$ or $6PbO.5PbUO_4$ (Sterns, 1967). On the other hand, it is stated in the literature on phases in the $PbO–PbSO_4$ system, notably $PbO.PbSO_4$ (Sahl, 1970) and $2PbO.PbSO_4$ (Sahl, 1981), that the structural principles of these phases, which contain no recognizable elements of the $PbSO_4$ (anglesite) structure, are better expressed by the formulae $Pb_2O(SO_4)$ and $Pb_3O_2(SO_4)$ respectively. In the former (lanarkite), OPb_4 tetrahedra, similar to those encountered in both forms of PbO, share two edges to form infinite chains of stoichiometry Pb_2O which are connected to discrete sulfate groups by longer Pb–O bonds. In $Pb_3O_2(SO_4)$, tetrahedra of the same kind share three edges resulting in chains of composition Pb_3O_2. A somewhat similar description, involving OPb_4 tetrahedra, is also possible for the Pb_3UO_6

Table 3. *Coordination around oxygen atoms* O(3) *and* O(4)

O(3)–Pb(1)	2·45 (1) Å	Pb(1)–O(3)–Pb(4)	100·1 (5)°
O(3)–Pb(4)	2·21 (1)	Pb(1)–O(3)–Pb(5)	104·7 (4) 2×
O(3)–Pb(5)	2·26 (1) 2×	Pb(4)–O(3)–Pb(5)	119·4 (3) 2×
O(3)–O(4)	2·87 (2)	Pb(5)–O(3)–Pb(5)	106·2 (5)
O(4)–Pb(2)	2·37 (1)	Pb(2)–O(4)–Pb(3)	109·0 (6)
O(4)–Pb(3)	2·28 (2)	Pb(2)–O(4)–Pb(5)	104·2 (4) 2×
O(4)–Pb(5)	2·36 (1) 2×	Pb(3)–O(4)–Pb(5)	118·8 (4) 2×
		Pb(5)–O(4)–Pb(5)	100·0 (5)

$(2PbO.PbUO_4)$ structure. The oxygen atoms O(3) and O(4) which do not participate in the octahedral oxygen environment of the uranium atoms are each surrounded tetrahedrally by four lead atoms (Fig. 2, Table 3) and the two tetrahedra share an edge, Pb(5)–Pb(5), 3·61 Å, forming the dimeric unit Pb_6O_2. The dimeric units include all lead atoms in the structure and are connected to the $(UO_5)_\infty$ chains of corner-sharing UO_6 octahedra by other, usually longer, Pb–O bonds. Considered in this way, the composition of the unit cell is $4Pb_6O_2.8UO_5$, corresponding to the formula Pb_3OUO_5 which may be structurally more informative than either Pb_3UO_6 or $2PbO.PbUO_4$.

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The Structure of Atacamite and its Relationship to Spinel

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Abstract. Atacamite, $Cu_2Cl(OH)_3$, $M_r = 213·6$, $F(000) = 408$, orthorhombic, *Pnma*, $a = 6·030$ (2), $b = 6·865$ (2), $c = 9·120$ (2) Å, $V = 377·5$ Å³, $Z = 4$, $D_x = 3·76$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 117·8$ cm⁻¹, $T = 293$ K. Non-H atoms refined anisotropically to $R = 0·029$ for 399 observed data with $I > 3\sigma(I)$. (The structure refined less satisfactorily in the alternative space group $Pna2_1$.) Cu atoms are in

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