

with a coordination number, including all oxygens at less than 3 Å, ranging from 3 to 5, and a number of bonds up to and often less than five. To the accuracy of the present data, Te(1) is situated at a centre of symmetry with six equivalent Te^{IV}-O bonds of 2.104 (7) Å and angles of 90 ± 0.5°. There is no indication, for example from the temperature factor, that Te(1) is at a site of too high symmetry, to be lowered by changing the space group from *R*3̄*m* to *R*3*m*. In fact, refining in *R*3*m* does not change the Te coordination to any significant extent, as would also hardly be conceivable for a near-cubic structure.

The authors are indebted to Professor Dr E. H. P. Cordfunke and Mr P. Van Vlaanderen of the Netherlands Energy Research Foundation ECN for preparation of the specimens and their great interest shown in the work, and to Mr D. Heijdenrijk for his untiring efforts to select samples and collect the X-ray data.

Acta Cryst. (1986). **C42**, 523–525

Redetermination of Tricalcium Uranate(VI). A Rietveld Refinement of Neutron Powder Diffraction Data

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(Received 11 September 1985; accepted 24 December 1985)

Abstract. Ca₃UO₆, *M_r* = 454.27, monoclinic, *P*2₁/*n*, *Z* = 2. At room temperature: *a* = 5.7292 (7), *b* = 5.9562 (7), *c* = 8.2991 (10) Å, β = 90.56 (1)°, *V* = 283.19 (6) Å³, *D_x* = 5.327 (1) Mg m⁻³, μ*R* = 0.14. The structure has been refined by Rietveld analysis of powder neutron diffraction data [λ = 2.5790 (3) Å, *R_{wp}* = 6.14%] for 136 reflections. The structure is of monoclinic, deformed CaTiO₃ type, with ordering of Ca and U in octahedral positions. The stability in water at 573 K and 0.2 GPa for 1 week was tested: it was found that Ca₃UO₆ is totally decomposed under these conditions.

Introduction. The preparation, crystal structure determination and solubility test in water at elevated temperatures and pressures form part of a research program to investigate compounds with perovskite or related structures for their properties as a host lattice for nuclear waste. Ca₃UO₆ is reported to adopt a monoclinic, deformed perovskite-like structure with space group *P*2₁ (Loopstra & Rietveld, 1969). In relation to other substituted perovskites this space group seems too low. The powder diffraction data

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suggest the space group *P*2₁/*n* in agreement with the powder diffraction data of Ca₃WO₆ (JCPDS file No. 22–541).

Experimental. AR starting materials CaCO₃ and U₃O₈ thoroughly mixed in an agate mortar in the appropriate ratio; mixture heated in a platinum crucible at 1073 K for 1 d and, after grinding, heated at 1473 K for one week with repeated grindings, and annealed one week at 1073 K.

X-ray powder diffraction pattern obtained with a Philips PW 1050 diffractometer; all lines could be indexed with a monoclinic unit cell, in accordance with electron diffraction data (Siemens Elmiskop 102 electron microscope, double tilt, lift cartridge, 100 kV). Lattice absences *h*0*l* *h*+*l*=2*n*+1 and 0*k*0 *k*=2*n*+1 in accordance with space group *P*2₁/*n*. Since no single crystals were available, Rietveld's (1969) method was used for refinement of neutron powder diffraction data; neutron powder profile recorded (room temperature, atmospheric pressure) at the Petten High-Flux Reactor; 5° < 2θ < 163° in steps of 0.1°; neutrons at room temperature from (111) planes of a Cu crystal;

Table 1. Fractional atomic coordinates and isotropic thermal parameters (\AA^2) of Ca_3UO_6 at room temperature

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Ca(1)	0.5151 (6)	0.5522 (4)	0.2430 (5)	1.2 (1)
Ca(2)	0.5	0.0	0.0	1.1 (1)
U	0.0	0.5	0.0	0.2 (1)
O(1)	0.1760 (4)	0.2141 (4)	-0.0802 (3)	0.6 (1)
O(2)	0.2948 (4)	0.6769 (4)	-0.0546 (3)	0.7 (1)
O(3)	0.3747 (4)	0.9324 (4)	0.2669 (3)	0.4 (3)

Table 2. Atomic distances (\AA) in Ca_3UO_6 at room temperature

Ca(1)–O(1)	2.344 (4)	Ca(2)–O(1)	2.343 (2)
–O(1)	2.635 (4)	–O(2)	2.298 (3)
–O(1)	3.165 (5)	–O(3)	2.370 (2)
–O(2)	2.861 (5)		
–O(2)	2.818 (4)	U–O(1)	2.091 (2)
–O(2)	2.351 (4)	–O(2)	2.045 (2)
–O(3)	2.412 (4)	–O(3)	2.096 (2)
–O(3)	2.345 (4)		

pyrolytic graphite with a total thickness of 120 mm as a second-order filter; Soller slits, horizontal divergence 0.5° , placed between the reactor and the monochromator and in front of each of the four ^3He counters; sample holder ($\varnothing = 19.44$ mm) consisted of a V tube, closed with Cu plugs fitted with O rings. No precautions to avoid preferred orientation. Maximum absorption correction 0.4%, $\mu R = 0.14$ (Weber, 1967). Background determined by extrapolation between those parts in the diagram containing no contribution or, for higher values of 2θ , only a small contribution, from reflections. The stability in water at 573 K and 0.2 GPa for 1 week was tested: it was found that Ca_3UO_6 is totally decomposed under these conditions.

The determined structure of Ca_3UO_6 (Loopstra & Rietveld, 1969) was used as a trial model with allowance for a translation ($-\frac{1}{4}, \frac{1}{2}, -\frac{1}{2}$) of the atomic parameters. Ca(1), O(1), O(2) and O(3) at (*x*, *y*, *z*); Ca(2) at ($\frac{1}{2}$, 0, 0) and U at ($0, \frac{1}{2}$, 0).

28 parameters in the refinement: a scale factor, three half-width parameters defining the Gaussian-like shape of the reflections, the counter zero error, the unit-cell parameters, the atomic positional parameters, isotropic thermal parameters and an asymmetry parameter.

Coherent scattering lengths: Ca 4.9, U 8.42, O 5.805 fm (Koester, Rauch, Herkens & Schroeder, 1981). The Rietveld program minimizes the function $\chi^2 = \sum w_i [y_i(\text{obs.}) - (1/c)y_i(\text{calc.})]^2$, where $y_i(\text{obs.})$ and $y_i(\text{calc.})$ are the observed and calculated data points, w_i is the statistical weight [$1/y_i(\text{obs.})$] allotted to each data point and *c* is the scale factor; $R_{wp} = 100[\sum w_i |y_i(\text{obs.}) - (1/c)y_i(\text{calc.})|^2 / \sum w_i |y_i(\text{obs.})|^2]^{1/2} = 6.14\%$, compared with 3.52% expected on purely statistical grounds. $\Delta/\sigma < 0.3$ in final cycle. E.s.d.'s calculated according to the original Rietveld formulation. Largest correlation matrix element for structural parameters 0.38.

Discussion. Atomic parameters are given in Table 1, atomic distances in Table 2. The agreement between the observed and calculated profile of the data is shown in Fig. 1.* Fig. 2 shows the projection of one layer of Ca_3UO_6 along [001].

* A list of numerical values corresponding to the data in Fig. 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42736 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

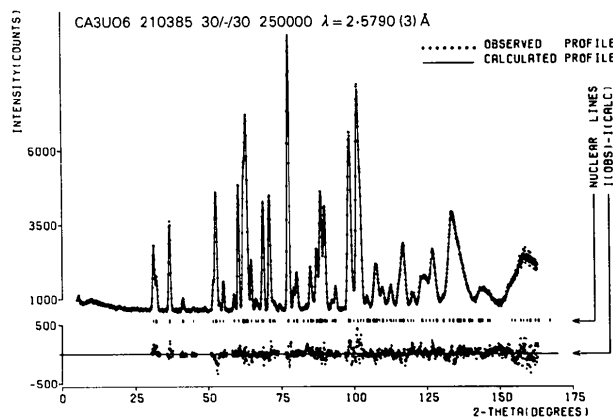


Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of Ca_3CaUO_6 at room temperature; a difference (observed–calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

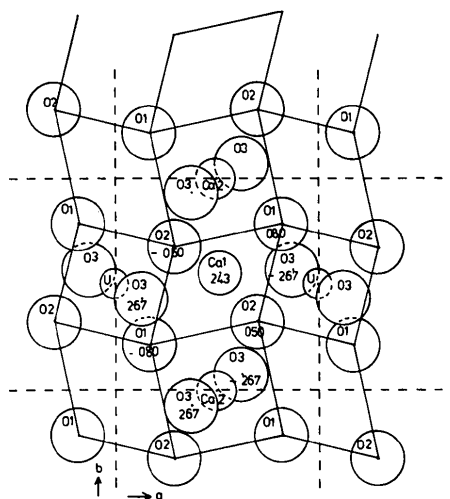


Fig. 2. Projection of one layer of Ca_3UO_6 along [001]. Fractional heights ($\times 10^3$) are indicated.

The structure can be described as a perovskite with regular CaO_6 and UO_6 octahedra. Each UO_6 octahedron shares corners with six CaO_6 octahedra and *vice versa*. The Ca(1) atoms are in bicapped trigonal prisms between the octahedra.

The UO_6 octahedra are smaller as are the $\text{Ca}(2)\text{O}_6$ octahedra. All octahedra are rotated around a fourfold axis parallel to [001] and a twofold axis parallel to [110] of the aristotype (Megaw, 1973). By analogy with Megaw's (1972) analysis for the $\text{GdFeO}_3(\text{CaTiO}_3)$ -type tilt system the rotation angles are ω about [001] and φ about [110] of the aristotype. Because of these rotations the coordination number of the Ca(1) atom has changed from 12 to 8 and the geometry is that of a bicapped trigonal prism. Because the octahedra are different in size the rotations are also different. From the positional parameters of O(1) and O(2) we calculate $\omega(\text{UO}_6)$ 13.70 (3), $\omega[\text{Ca}(2)\text{O}_6]$ 12.05 (3), $\varphi(\text{UO}_6)$ 22.19 (3) and $\varphi[\text{Ca}(2)\text{O}_6]$ 21.13 (3)°. The mean U—O, Ca(1)—O and Ca(2)—O distances are respectively 2.08, 2.62 and 2.34 Å, which are in agreement with the sum of the ionic radii found in the literature: 2.13, 2.52, 2.40 Å respectively (Shannon & Prewitt, 1969). The structure is nearly the same as is reported by Loopstra & Rietveld (1969).

The same structure type is found in CaTiO_3 and CaZrO_3 (Koopmans, van de Velde & Gellings, 1983),

but the ordering of the octahedra lowers the space-group symmetry from $Pbnm$ to $P2_1/n$.

Ringwood (1978) stated that in Synroc the U is present in the zirconolith phase. There is, however, a possibility that the U is also present in a perovskite-like phase as Ca_3UO_6 . In that case an increased leaching of U is likely.

The authors are indebted to Mr J. F. Strang and Dr R. B. Helmholtz of the Energie-onderzoek Centrum Nederland (Petten) for the collection of the neutron diffraction data.

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Acta Cryst. (1986). C42, 525–528

Structure of an Oxonium Iron(III) Orthophosphate Hydrate

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(Received 26 August 1985; accepted 12 November 1985)

Abstract. Triiron(III) oxonium tetradecahydrogenodotriacontaoxooctaphosphate tetrahydrate, $(\text{H}_3\text{O})\text{Fe}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_6 \cdot 4\text{H}_2\text{O}$, $M_r = 1030.6$, monoclinic, $C2/c$, $a = 16.797$ (8), $b = 9.528$ (8), $c = 17.609$ (9) Å, $\beta = 90.64$ (6)°, $V = 2818$ (3) Å³, $Z = 4$, $D_x = 2.43$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 21.7$ cm⁻¹, $F(000) = 2067.8$, $T = 290$ K, final conventional R factor = 0.091, $wR = 0.099$ for 986 unique reflections and 218 variables. This analysis and Mössbauer spectroscopy led to the formula $(\text{H}_3\text{O})\text{Fe}_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_6 \cdot 4\text{H}_2\text{O}$. In the structure, iron(III) orthophosphate layers perpendicular to the c axis

alternate with water layers. The iron phosphate layers contain FeO_6 octahedra which share vertices with $\text{O}_2\text{P}(\text{OH})_2$ and $\text{O}_3\text{P}(\text{OH})$ tetrahedra. Within this network are hollows that are occupied by oxonium ions. The pseudo symmetry of the layer is well described by the layer symmetry group $3p21$. Neighbouring layers are connected by hydrogen-bonded water molecules. Fe—O distances vary from 1.94 (2) to 2.06 (2) Å. The present compound is isostructural with analogous thallium and aluminium orthophosphates.

Introduction. Iron phosphates are of importance in many technological and ecological areas, such as corrosion inhibition in systems carrying water, the interaction of phosphates as adhesives on iron and steel,

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