

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.

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Structure of an Oxonium Iron(III) Orthophosphate Hydrate

BY W. P. BOSMAN, PAUL T. BEURSKENS, J. M. M. SMITS, H. BEHM, J. MINTJENS, W. MEISEL* AND J. C. FUGGLE
Crystallography Laboratory and Department of Molecular Spectroscopy, Research Institute for Materials, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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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,

* Present address: Institute of Inorganic Chemistry, University of Mainz, D-6500 Mainz, Federal Republic of Germany.

and the interaction of soil components (e.g. goethite, $\alpha\text{-FeOOH}$) with fertilizers containing phosphates. Despite this importance little is known about the structural chemistry of the iron phosphates. Even orthophosphoric acid is very complex and contains a large assortment of linear and cyclic oligomers based on P—O—P bridges (Van Wazer, 1958, 1961). As many of the iron phosphate compounds occurring in technological problems are almost insoluble and unstable at high temperatures, preparation of single crystals is difficult and most attempts at characterization have been attempted by methods like Mössbauer spectroscopy (see e.g. Meisel, Guttman & Gütlich, 1983). Thus when we found small single crystals of the present compound in the reaction products of iron with phosphoric acid, we decided to elucidate the structure by X-ray analysis.

Experimental. Compound prepared by reaction of 4.5 g iron powder ($\alpha\text{-Fe}$) with 50 ml 85% H_3PO_4 . Reaction vessel was allowed to stand for eleven weeks at room temperature without stirring. The pale pink-grey precipitate formed contained small crystals. Mössbauer spectra indicated presence of only Fe^{III} in the sample (Meisel, Ten Dolle, Mintjes, Fuggle, Bosman & Beurskens, 1986).

Irregular crystal $0.15 \times 0.12 \times 0.03$ mm selected for X-ray analysis. Mo $K\alpha$ radiation, graphite-crystal monochromator, Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions determined from angular settings of 25 reflections with $5 < \theta < 18^\circ$. Space group $C2/c$ from systematic absences and structure determination. Intensity data of 9898 reflections (full sphere up to $\theta = 25^\circ$) measured, using ω - 2θ scan technique, scan angle 1.90° and variable scan rate with max. scan time 20 s per reflection. Intensity of primary beam checked throughout data collection by monitoring three reference reflections every 30 min. Decline in intensities up to 29%, probably due to decomposition, occurred over course of data collection. Smooth curve based on reference reflections used to correct for this drift. On all reflections, profile analysis performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction applied using ψ scans (North, Phillips & Mathews, 1968). (Correction factors in the range 0.77 to 1.00; analytical absorption corrections could not be performed because of irregular shape of crystal.) Space-group-symmetry-equivalent reflections averaged, $R_{\text{int}} = 0.12$, resulting in 2419 unique reflections of which 986 observed with $I > 3\sigma(I)$ and $R_{\text{int}} = 0.04$. No extinction correction. Lorentz and polarization corrections applied and data reduced to $|F_o|$ values. The three iron atoms found using Patterson techniques (*SHELX84*; Sheldrick, 1984). P and O atoms found with *DIRDIF* (Beurskens *et al.*, 1982). Structure refined by full-matrix least squares on $|F|$ values, using *SHELX76* (Sheldrick, 1976). Scatter-

ing factors from *International Tables for X-ray Crystallography* (1974). Isotropic refinement converged to $R = 0.119$. At this stage empirical absorption correction applied (Walker & Stuart, 1983), resulting in further decrease of R to 0.104 (correction factors in range 0.876–1.143). During final stages of refinement positional parameters and anisotropic thermal parameters of all atoms refined. Location of hydrogen atoms not possible, due to quality of data and probable disorder of positions. Final conventional agreement factors were $R = 0.091$ and $wR = 0.099$ for 986 observed reflections and 218 variables. High R factor due to quality of crystal. Function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.0004 F_o^2]$ with $\sigma(F_o)$ from counting statistics. Max. shift over e.s.d. ratio in last full-matrix least-squares cycle less than 0.01. Final difference Fourier map showed no peaks higher than $1.0 e \text{ \AA}^{-3}$. Plots made with *PLUTO* (Motherwell, 1976).

Table 1. Atomic parameters (with e.s.d.'s)

	x	y	z	$U_{\text{eq}}(\text{\AA}^2 \times 100)$
Fe(1)	0.29057 (24)	0.4728 (4)	0.24444 (26)	1.58 (17)
Fe(2)	$\frac{1}{2}$	0.8430 (6)	$\frac{1}{2}$	1.36 (23)
P(1)	0.3365 (4)	0.7619 (7)	0.3434 (4)	1.4 (3)
O(11)	0.3487 (9)	0.6130 (16)	0.3135 (11)	1.2 (7)
O(12)	0.4037 (10)	0.8618 (16)	0.3169 (12)	2.2 (8)
O(13)	0.2553 (10)	0.8165 (20)	0.3231 (12)	2.5 (9)
O(15)	0.3461 (10)	0.7587 (20)	0.4315 (9)	2.4 (8)
P(2)	0.4427 (4)	0.5649 (7)	0.1441 (5)	2.1 (3)
O(21)	0.3881 (10)	−0.5304 (20)	0.1841 (12)	3.0 (9)
O(22)	0.4570 (13)	0.7043 (22)	0.1816 (13)	5.3 (10)
O(24)	0.5243 (12)	0.4846 (23)	0.1290 (14)	5.6 (11)
O(25)	0.4070 (12)	0.5841 (22)	0.0581 (12)	4.3 (10)
P(3)	0.1276 (4)	0.5134 (7)	0.3535 (5)	2.2 (3)
O(31)	0.1977 (10)	0.4789 (21)	0.3119 (13)	3.3 (9)
O(32)	0.0497 (10)	0.4952 (19)	0.3111 (11)	2.1 (8)
O(34)	0.1323 (12)	0.6722 (19)	0.3803 (12)	3.7 (9)
O(35)	0.1231 (15)	0.4357 (20)	0.4352 (13)	7.1 (12)
P(4)	0.3187 (5)	0.2066 (8)	0.3548 (5)	2.4 (3)
O(41)	0.3447 (11)	0.3195 (18)	0.3047 (12)	2.7 (9)
O(43)	0.2523 (11)	0.1149 (17)	0.3251 (11)	2.4 (8)
O(44)	0.3957 (10)	0.1136 (21)	0.3737 (11)	2.9 (9)
O(45)	0.2962 (13)	0.2638 (23)	0.4310 (12)	4.6 (11)
O(1)	0	0.766 (3)	$\frac{1}{2}$	9.6 (23)
O(2)	0.2218 (13)	0.0457 (28)	0.0012 (16)	7.7 (14)
O(3)	0.4959 (14)	0.8012 (24)	−0.0013 (14)	6.8 (11)

Table 2. Selected averaged distances (\AA) and angles ($^\circ$)

Type	Range	Average	Number of terms	Standard deviation (r.m.s. deviation of the mean)
Fe—O(P)	1.93–2.05	1.995	9	0.015
P—O(Fe)	1.43–1.55	1.498	9	0.012
P—O(H)	1.51–1.63	1.587	7	0.016
O(Fe)—Fe—O(Fe)	84.3–97.5	90	15	1.0
O(Fe)—P—O(Fe)	111.5–116.3	113.8	6	0.9
O(Fe)—P(1)—O(H)	104.3–109.0	107.2	3	1.5
O(Fe)—P(d)—O(H)	106.8–113.4	109.6	12	0.6
O(H)—P(d)—O(H)	100.1–103.2	101.7	3	0.9

Discussion. Final positional and thermal parameters are given in Table 1.* The most important averaged distances and angles are given in Table 2.

A projection of the iron phosphate layer along the *c* axis is given in Fig. 1. The formula of the present compound is partly based on neutrality requirements with all iron as Fe^{III}. It fits very well with the general discussions given for orthophosphates of composition (H₃O, Na, K, NH₄)(Fe,Al)₃H₁₄(PO₄)₈·4H₂O (Remy & Boule, 1971; d'Yvoire, 1961, 1962), and with the structures of the isostructural thallium (Chiadmi, Vicat, Tran Qui & Boudjada, 1985) and aluminium (Brodalla & Kniep, 1980) compounds, compared below.

The present structure consists of iron orthophosphate layers perpendicular to the *c* axis, which alternate with water layers. The iron phosphate layers contain FeO₆ octahedra which share vertices with O₂P(OH)₂ and O₃P(OH) tetrahedra. Within this network are hollows which are occupied by oxonium ions. The iron and oxonium in one layer are positioned at *z* = 0.25 (and *z* = 0.75 for the symmetry-related layer). Neighbouring layers are connected by hydrogen-bonded water molecules, positioned around *z* = 0.0 and around *z* = 0.5.

P(1) is a monohydrogenphosphate and we use P(*d*) for dihydrogenphosphate groups [atoms P(*d*), *d*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42712 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

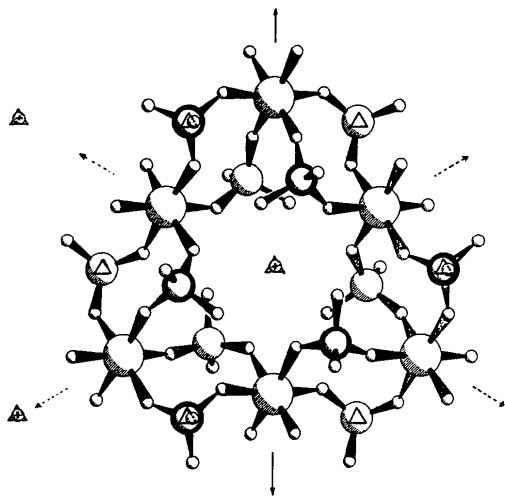


Fig. 1. Projection of the oxonium iron phosphate layer along the *c* axis. Fe=large circles (*z*=0.25); P=medium circles (heavy circles for *z*=0.35); O=small circles (+ = oxonium). Triangles [on P(*d*) and oxonium] indicate pseudo threefold axes; arrows indicate twofold axes (solid: parallel *b*; dotted: pseudo).

Table 3. Atomic sites of Fe, P and oxonium with 3*p*21 layer symmetry

	(Symm = point group.)		
	Symm	Mult	Position
Fe	2	3	0, <i>y</i> , 0
P(1)	3	2	$\frac{1}{3}, \frac{2}{3}, z$
P(<i>d</i>)	1	6	<i>x</i> , <i>y</i> , <i>z</i>
H ₃ O	32	1	0, 0, 0

= 2,3,4]. P(1) and P(*d*) tetrahedra are bonded to three and two different iron atoms, respectively. Each iron atom is connected with three neighbouring iron atoms; each connection is by one P(1) and one P(*d*) tetrahedron. The oxygen atoms, bridging between P(*i*) and Fe, are denoted O(*ij*), *j*=1,3. One of the faces of the P(1) tetrahedron is parallel to the iron phosphate layer, while the OH group [atom O(15)] points out of this layer. The P(*d*) tetrahedra are similarly oriented but slightly tilted, with one OH [atoms O(*i*4)] in the base and one OH [atoms O(*i*5)] pointing out of the layer. All tetrahedra are alternately oriented with their tops [atoms O(*i*5)] up and down with respect to the layer: these tops penetrate in the water layers around *z* = 0.0 and *z* = 0.5.

By space-group symmetry, an individual iron phosphate layer contains a twofold axis, but the local symmetry of each layer is considerably higher. The layer symmetry group (*Schichtgruppe*; Niggli, 1959) of such a layer is 3*p*21. This layer can be described in a two-dimensional unit cell with *a* = *b* = 9.6 Å and *γ* = 120°. The (three-dimensional) general positions, with the origin at the oxonium position, are

$$\begin{array}{lll} x, y, z; & -y, x-y, z; & y-x, -x, z; \\ y, x, -z; & -x, y-x, -z; & x-y, -y, -z. \end{array}$$

Atomic sites of Fe, P and oxonium with 3*p*21 layer symmetry are given in Table 3. The threefold axis of this layer is approximately maintained in the water layer, but threefold axes of neighbouring layers (*z* = 0.25 and *z* = -0.25) do not coincide. There are many possible hydrogen bonds in and around the water layers, but the quality of our data did not permit the location of the hydrogen atoms.

The present oxonium iron orthophosphate is isostructural with Al₃{H₃O}H₁₄(PO₄)₈·4H₂O (Brodalla & Kniep, 1980), and also with Tl₃(Tl_{0.5}H₃O_{0.5})H₁₄(PO₄)₈·4H₂O (Chiadmi *et al.*, 1985). In the former structure, hydrogen atoms were located. In the latter structure, the oxonium position is occupied by oxonium and thallium(I) in 1:1 disorder. Otherwise we see no structural differences (The thallium structure has been refined in space group *P* $\bar{1}$; by **a** = -**a'**-2**b'**, **b** = -**a'**, **b** = 9.820, *c* = 17.870 Å, *a* = 90.01, *β* = 90.167, *γ* = 90.03°; atomic positions, after the corresponding transformation, obey *C*2/*c* symmetry.)

During our chemical investigations, by heating and by precipitation from solutions of different concentrations, we have obtained crystalline iron phosphates with less water (Meisel *et al.*, 1986). The structure of such materials remains to be investigated.

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Structures of Tetrathallium(I) Tetrathiosilicate(IV) and Tetrathallium(I) Tetraselensilicate(IV)

BY G. EULENBERGER

Institut für Chemie der Universität Hohenheim, Garbenstraße 30, D-7000 Stuttgart 70, Federal Republic of Germany

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Abstract. $\text{Tl}_4[\text{SiS}_4]$, $M_r = 973.8$, monoclinic, Cc , $a = 12.518$ (3), $b = 11.241$ (2), $c = 7.567$ (2) Å, $\beta = 112.80$ (2)°, $V = 981.4$ (4) Å³, $Z = 4$, $D_x = 6.59$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 668$ cm⁻¹, $F(000) = 1608$, room temperature, final $R = 0.066$ for 883 observed unique reflections. $\text{Tl}_4[\text{SiSe}_4]$, $M_r = 1161.4$, monoclinic, $C2/c$, $a = 11.664$ (9), $b = 7.277$ (4), $c = 24.903$ (12) Å, $\beta = 99.93$ (5)°, $V = 2082$ (2) Å³, $Z = 8$, $D_x = 7.41$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 772$ cm⁻¹, $F(000) = 3792$, room temperature, final $R = 0.064$ for 866 observed unique reflections. $\text{Tl}_4[\text{SiS}_4]$ is isostructural with $\text{Tl}_4[\text{GeS}_4]$ and contains $[\text{SiS}_4]^{4-}$ anions held together by Tl^+ cations in irregular sixfold coordination. The relations between the structures of $\text{Tl}_4[\text{SiS}_4]$, tetragonal $\text{Na}_4[\text{SnS}_4]$, and $\text{Tl}_4[\text{SnS}_4]$ are discussed. $\text{Tl}_4[\text{SiSe}_4]$ is built up from slabs parallel to (001) which consist of almost planar 3⁶ nets of Tl^+ cations enclosed between two parallel layers of

$[\text{SiSe}_4]^{4-}$ tetrahedra. Further Tl^+ cations are located in voids between the $[\text{SiSe}_4]^{4-}$ tetrahedra of each layer and between the slabs. The Tl atoms in three general and two special positions are coordinated to essentially six, five, and four Se atoms. The lone pairs of 6s electrons of univalent thallium exhibit strong stereochemical effects with two of the Tl atoms. The pseudohexagonal properties of the structure are described by means of a group-subgroup relation to a hypothetical hexagonal aristotype.

Introduction. In the Tl–Si–S and Tl–Si–Se systems, the phases $\text{Tl}_4[\text{Si}_2\text{S}_6]$ and $\text{Tl}_4[\text{Si}_2\text{Se}_6]$ have been prepared and structurally characterized (Eulenberger, 1982). The two compounds adopt the $\text{Tl}_4[\text{Ge}_2\text{S}_6]$ structure (Eulenberger, 1978). Further investigations on the same systems led to the synthesis of $\text{Tl}_4[\text{SiS}_4]$ and $\text{Tl}_4[\text{SiSe}_4]$ (Eulenberger, 1984a). It appeared to be of interest to