A New Uranium(VI) Monophosphate with a Layered Structure: $Ba_3[UO_2(PO_4)(PO_3(OH))]_2{\cdot}xH_2O$ ($x \approx 0.4$)

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A new uranium(VI) phosphate containing barium has been synthesized hydrothermally: $Ba_3[UO_2(PO_4)(PO_3(OH))]_2{\cdot}xH_2O$ ($x \approx 0.4$). The structure determination and refinement have been performed using single-crystal X-ray diffraction in the $P2_1/c$ space group with the cell parameters $a = 9.5316(7)$ Å, $b = 8.7323(6)$ Å, $c = 10.5646(10)$ Å, $\beta = 97.439(7)°$, $V = 873.9(1)$ Å^3, and $Z = 2$. The presence of hydroxyl groups and water molecules in the structure has been evidenced by IR and TGA studies. The U−P−O host lattice consists of puckered layers resulting from the connection of UO_7 pentagonal bipyramids and monophosphate groups; the barium cations are distributed over two sites between these layers.

Introduction

The ability of some mineral compounds to play the role of host matrix for actinides, combined with their great resistance to corrosion, have led to consideration of crystalline oxides as an alternative solution to glasses in the field of nuclear waste storage. The $LnPO_4$ monazite type structure, for example, presents these features and has been studied as a host matrix for nuclear waste lanthanides and actinides.[1] From this point of view, uranium and thorium phosphates may be considered as very interesting materials, especially if they can be synthesized easily. Recently, the structure of several actinide phosphates has been examined[2] (see, for example, $U(UO_2)(PO_4)_2$,[3] $Th_4(PO_4)_4P_2O_7$,[4] or the organically templated phosphates $[NHEt_3][(UO_2)_2(PO_4)(HPO_4)]$ and $[NPr_4][(UO_2)_3(PO_4)(HPO_4)_2]$[5] and ref 6 for a review of uranium(VI) compounds). To find new phosphate matrixes that could contain actinide atoms, we have undertaken the investigation of A−U−P−O systems, A being a monovalent or a divalent cation. We report here on the synthesis and on the structure of a new uranium(VI) phosphate containing barium: $Ba_3[UO_2(PO_4)(PO_3(OH))]_2{\cdot}xH_2O$ (with $x \approx 0.4$).

Experimental Section

Crystal Growth and Chemical Synthesis. The single crystal used for the structure determination was extracted from a preparation synthesized in the following way: first, $BaCO_3$ (Prolabo, purity 99%), $H(NH_4)_2PO_4$ (Prolabo, purity 99%), and UO_2 (Cerac, purity 99.8%) were mixed in an agate mortar (molar ratios 2:8:1.2) and heated in a platinum crucible for 3 h at 673 K in order to decompose the ammonium phosphate and the barium carbonate. The resulting product was ground and placed with water (molar ratio 222) in a 25 cm^3 Teflon-lined autoclave which was heated for 20 h at 493 K and cooled at 2.5 K/h to 293 K. The resulting mixture was filtered off, washed with water, and air-dried at ambient temperature. An unidentified green powder containing some yellow plates of the title compound was thus obtained.

The synthesis of $Ba_3[UO_2(PO_4)(PO_3(OH))]_2{\cdot}xH_2O$ as a pure powder sample was performed hydrothermally from a mixture of $Ba(OH)_2{\cdot}8H_2O$ (Prolabo, purity 99%), H_3PO_4 (Prolabo, 75%), $(NO_3)_2UO_2{\cdot}6H_2O$ (Merck, purity 99%), and H_2O (molar ratios: 3:4:2:111) in a Teflon-lined autoclave heated for 20 h at 493 K and cooled at 2.6 K/h to 293 K. The resulting mixture was filtered off, washed with water, and air-dried at ambient temperature. A yellow powder containing yellow plates was obtained; its powder X-ray diffraction pattern was indexed in a monoclinic cell, in agreement with the parameters resulting from the single-crystal X-ray study (Table 1).

Energy Dispersive Analysis (EDS). The elementary analysis of the Ba, U, and P elements was performed with a Tracor microprobe mounted on a JEOL 840 scanning electron microscope. It led to the $\ll Ba_3U_2P_4 \gg$ composition, which was confirmed by the structure determination.

Structure Determination. Several crystals were selected optically and tested by the oscillation and Weissenberg methods using Cu Kα radiation. A yellow single crystal with dimensions $0.154 \times 0.077 \times 0.039$ mm^3 was then chosen for the structure determination. The cell parameters reported in Table 1 were determined and refined by diffractometric techniques at 293 K with a least-squares method based upon 25 reflections in the range $18° < \theta < 22°$. The data were collected on a CAD4 Enraf Nonius diffractometer with the data collection parameters reported in Table 1. The reflections were corrected for Lorentz and polarization effects, for absorption (Gaussian method), and for secondary extinction.[7]

The structure was solved with the heavy atom method in the $P2_1/c$ space group, in agreement with the observed systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$.

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Table 1. Summary of Crystal Data, Intensity Measurements and Structure Refinement Parameters for $Ba_3[UO_2(PO_4)(PO_3(OH))]_2 \cdot xH_2O$

Crystal Data	
space group	$P2_1/c$
cell dimensions	$a = 9.5316(7)$ Å
	$b = 8.7323(6)$ Å
	$c = 10.5646(10)$ Å
	$\beta = 97.439(7)°$
volume (Å)^3	873.9(1)
Z	2
ρ_{calc} (g·cm^{-3})	5.1
Intensity Measurements	
λ(Mo Kα)	0.71073
scan mode	$\omega-\theta$
scan width (deg)	$1.10 + 0.35 \tan \theta$
slit aperture (mm)	$1.0 + \tan \theta$
max θ (deg)	45
standard reflections	3 measured every 3600 s
measured reflections	7746
reflections with $I > 3\sigma$	4041
μ (mm^{-1})	25.65
Structure Solution and Refinement	
parameters refined	134
agreement factors	$R = 0.027$, $R_w = 0.029$
weighting scheme	$w = 1/\sigma^2$
Δ/σ max	$<0.4 \times 10^{-3}$

Table 2. Positional Parameters and Their Estimated Standard Deviations in $Ba_3[UO_2(PO_4)(PO_3(OH))]_2 \cdot xH_2O^a$

atom	x	y	z	$U \times 100$ (Å^2)
U	0.16167(2)	0.21698(2)	0.18828(2)	0.829(4)
Ba(1)	1/2	0	0	0.987(9)
Ba(2)	0.80685(3)	0.17872(4)	0.41363(3)	1.575(8)
P(1)	0.8678(1)	−0.0313(1)	0.1160(1)	0.79(3)
P(2)	0.5258(1)	0.3313(1)	0.1715(1)	0.91(3)
O(1)	0.0283(4)	0.3394(4)	0.3404(3)	1.16(9)
O(2)	0.2601(4)	0.4381(5)	0.3115(4)	1.45(9)
O(3)	0.1808(4)	0.0319(4)	0.0278(3)	1.33(9)
O(4)	−0.0694(4)	0.1270(4)	0.1530(4)	1.38(9)
O(5)	0.3922(4)	0.2314(5)	0.1495(5)	2.4(1)
O(6)	0.4694(5)	0.4987(5)	0.1294(4)	2.0(1)
O(7)	0.6281(4)	0.2747(4)	0.0848(4)	1.56(9)
O(8)	0.5859(5)	0.3367(5)	0.3094(4)	1.9(1)
O(9)	0.1014(4)	0.3619(4)	0.0715(4)	1.6(1)
O(10)	0.2149(4)	0.0790(5)	0.3092(4)	1.9(1)

[a] All atoms were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter defined as: $U = 1/3(u_{11} + u_{22} + u_{33})$.

The refinement of the atomic coordinates and of the anisotropic thermal factors of all atoms led to $R = 0.027$ and $R_w = 0.029$ and to the atomic parameters listed in Table 2 (anisotropic thermal factors are available on request from the author). The calculations were performed on a SPARK station with the XTAL 3.2 program.[7]

An analysis of the electrostatic bond strengths was performed using the Brese and O'Keeffe relation[8] for the Ba(II), U(VI), and P(V) species ($r_{ij} = 2.29$, 2.075, and 1.604, respectively). These calculations have shown a lack of electrostatic valence of about 0.85 for the oxygen atom O(6), suggesting the presence of an hydrogen atom. Despite the good accuracy of the structure refinement, the single-crystal X-ray diffraction study did not allow the localization of either the hydrogen atoms or the water molecules mentioned in the formula, although the IR and TGA studies showed without any ambiguity their existence.

Infrared Study and Thermogravimetric Analysis. The IR study confirmed the valence calculation results: the presence of hydroxyl groups in the title compound was indeed evidenced by the IR spectra recorded at room temperature and at 673 K with a Nicolet Magna 550 FT-IR spectrometer.

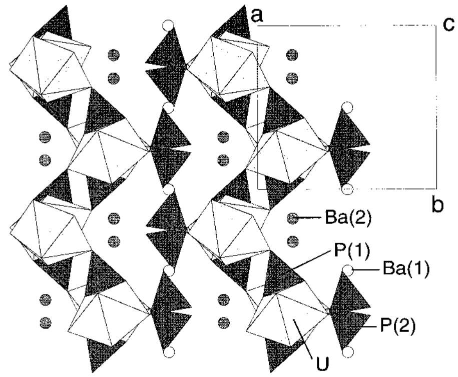

Figure 1. Projection of the structure along [001].

Thermogravimetric analysis (TGA) was also performed, using a Setaram microbalance with about 100 mg of powdered sample placed in a platinum crucible. In a first experiment, the sample was heated from room temperature to 1073 K in an argon atmosphere with a heating rate of 1 K/min. The corresponding TGA diagram showed two weight loss steps. The first one, which is not very important (0.47%) but continuous from 373 to 773 K is analyzed below; the second one (1.38%) occurs between 773 and 973 K: it is in agreement with the expected value of 1.35% and thus confirms the presence of two OH groups per formula unit in the studied phase. Note that the powder X-ray diffraction performed on the sample after this TGA evidenced an alteration of the structure (the identification of the derived phase is in progress). The first weight loss we mentioned above could be attributed to the presence of about 0.35 water molecule per formula unit in the structure. FTIR spectrum collected at 673 K also suggests water removal with respect to the measurement performed at room temperature. To verify this hypothesis, a second TGA was undertaken, the sample being heated in air at 1 K/min up to 773 K and then cooled to room temperature. The observed weight loss (0.52%) was similar to that obtained from the first TGA, i.e., corresponding to 0.39 water molecule per formula unit. Moreover, this experiment showed the reversible character of the hydration: the material loses H_2O from 373 to 773 K and reabsorbs atmospheric water at room temperature.

Description of the Structure

The projection of the structure along $\vec{c}$ (Figure 1) shows that its host lattice is built from monophosphate groups and UO_7 pentagonal bipyramids forming $[UO_2(PO_4)(PO_3(OH))]_\infty$ puckered layers stacked along $\vec{a}$. The barium cations sit between these layers, ensuring the cohesion of the structure.

As shown in Figure 2, which gives the projection of the structure along $\vec{a}$, each $[UO_2(PO_4)(PO_3(OH))]_\infty$ puckered layer can be described as the assemblage along $\vec{b}$ of $[UO_4(PO_4)]_\infty$ zigzag chains running along $\vec{c}$. In these chains one $P(1)O_4$ tetrahedron alternates with one UO_7 bipyramid as follows: each UO_7 bipyramid shares one edge with a P(1) tetrahedron and one apex with the next P(1) tetrahedron. Two successive $[UO_4(PO_4)]_\infty$ chains are enantiomorphic with respect to each other and linked along $\vec{b}$ through the apexes of their polyhedra, the P(1) tetrahedra of one chain sharing one apex with the UO_7 bipyramids of the adjacent chain. Thus the P(1) tetrahedra and the UO_7 bipyramids form $[UO_3(PO_4)]_\infty$ puckered layers on which the $P(2)O_3(OH)$ tetrahedra are connected to form the $[UO_2(PO_4)(PO_3(OH))]_\infty$ puckered layer. In fact, each P(2) tetrahedron shares only one apex with a UO_7 bipyramid and has three free

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Table 3. Distances (Å) and Angles (deg) in $Ba_3[UO_2(PO_4)(PO_3((OH))]_2 \cdot xH_2O$[a]

U	O(1)	O(2)	O(3)	O(4)	O(5)	O(9)	O(10)
O(1)	**2.423(4)**	2.427(5)	4.633(6)	2.784(5)	4.335(6)	3.018(6)	2.932(6)
O(2)	59.8(1)	**2.447(4)**	4.642(6)	4.322(5)	2.886(6)	2.858(5)	3.165(6)
O(3)	150.7(1)	149.4(1)	**2.366(4)**	2.990(6)	2.842(6)	3.030(5)	2.976(5)
O(4)	71.8(1)	130.0(1)	79.2(1)	**2.322(4)**	4.497(5)	2.821(6)	3.013(5)
O(5)	133.8(1)	75.0(2)	75.2(2)	154.2(2)	**2.290(4)**	3.012(6)	2.866(6)
O(9)	89.8(2)	82.9(2)	92.1(2)	85.2(2)	93.8(2)	**1.809(4)**	3.589(5)
O(10)	87.0(2)	95.7(2)	90.6(2)	93.6(2)	88.6(2)	176.8(2)	**1.781(4)**

P(1)	O(1^{i})	O(2^{i})	O(3^{ii})	O(4^{iii})
O(1^{i})	**1.533(4)**	2.427(5)	2.560(5)	2.542(5)
O(2^{i})	104.1(2)	**1.545(4)**	2.512(5)	2.519(5)
O(3^{ii})	113.4(2)	109.6(2)	**1.530(4)**	2.485(5)
O(4^{iii})	111.8(2)	109.6(2)	108.3(2)	**1.537(4)**

P(2)	O(5)	O(6)	O(7)	O(8)
O(5)	**1.536(4)**	2.465(6)	2.463(6)	2.510(6)
O(6)	103.6(2)	**1.601(4)**	2.554(6)	2.510(6)
O(7)	108.1(2)	110.6(2)	**1.505(4)**	2.516(6)
O(8)	111.8(3)	108.3(2)	114.0(2)	**1.495(4)**

Ba(1)−O(2^{i}) = 2.882(4)
Ba(1)−O(2^{iv}) = 2.882(4)
Ba(1)−O(3^{ii}) = 3.107(4)
Ba(1)−O(3) = 3.107(4)
Ba(1)−O(5^{ii}) = 2.838(5)
Ba(1)−O(5) = 2.838(5)
Ba(1)−O(7^{ii}) = 2.787(4)
Ba(1)−O(7) = 2.787(4)
Ba(1)−O(8^{i}) = 2.680(4)
Ba(1)−O(8^{iv}) = 2.680(4)

Ba(2)−O(1^{iii}) = 2.729(4)
Ba(2)−O(2^{i}) = 3.176(4)
Ba(2)−O(3^{v}) = 3.145(4)
Ba(2)−O(4^{iii}) = 3.166(4)
Ba(2)−O(4^{vi}) = 3.145(4)
Ba(2)−O(6^{i}) = 3.050(4)
Ba(2)−O(7^{vii}) = 2.672(4)
Ba(2)−O(8) = 2.637(4)
Ba(2)−O(9^{i}) = 2.899(4)
Ba(2)−O(9^{vi}) = 3.094(4)

[a] Symmetry codes: (i) $1 - x, -1/2 + y, 1/2 - z$; (ii) $1 - x, -y, -z$; (iii) $1 + x, y, z$; (iv) $x, 1/2 - y; 1/2 + z$; (v) $1 - x, 1/2 + y, 1/2 - z$; (vi) $1 + x, 1/2 - y, 1/2 + z$; (vii) $x, 1/2 - y, 1/2 + z$.

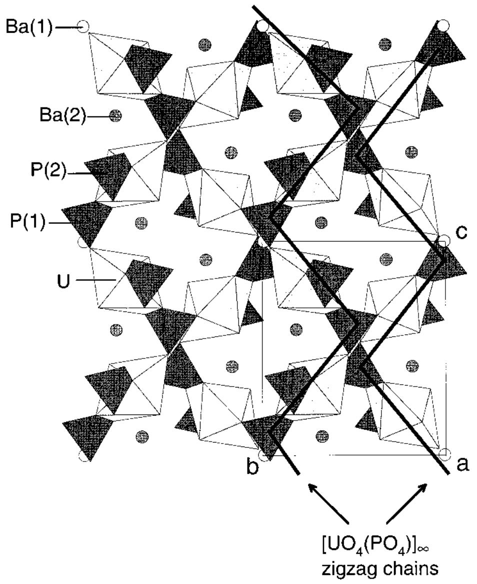

Figure 2. Projection of the structure along [100].

corners. Moreover the P(2) tetrahedra connected to one $[UO_4(PO_4)]_\infty$ chain sit all on the same side of the chain, i.e., are all in the cis-position with respect to it. As a consequence, due to the enantiomorphism of two successive chains, the rows of P(2) tetrahedra running along $\vec{c}$ are alternatively above and below the mean plane of the $[UO_3(PO_4)]_\infty$ puckered layer. Note that the $[UO_2(PO_4)(PO_3(OH))]_\infty$ layers can also be described by the assemblage of $[UO_4(PO_4)]_\infty$ zigzag chains running along $\vec{b}$. It is remarkable that in these chains the UO_7 bipyramids and the P(1) tetrahedra are linked in the same way as along $\vec{c}$. Nevertheless, the geometry of these chains is fundamentally different: the UO_7 bipyramids are practically aligned along $\vec{c}$, whereas they are in a zigzag configuration along $\vec{b}$.

The geometry of the UO_7 pentagonal bipyramid is similar to that observed in other compounds containing uranium with this rather usual 7-fold coordination. It presents on one hand five U−O distances ranging from 2.290(4) to 2.447(4) Å, which correspond to the five oxygen atoms of the equatorial plane of the bipyramid (Table 3). One can notice the short O(1)−O(2) distance of 2.427(5) Å that corresponds to the shared-edge of the UO_7 bipyramid with the $P(1)O_4$ tetrahedron. On the other hand, there are the two remaining very short U−O distances which correspond to the two ≪free≫ apical apexes O(9) and O(10) of the UO_7 bipyramid. The U−O(9) and U−O(10) bond distances present respective values of 1.809(4) and 1.781(4) Å and the O(9)−U−O(10) angle is of 176.8(2)°. These geometric features are thus consistent with the existence of a $(UO_2)^{2+}$ uranyl group and consequently with a +6 oxidation state for uranium, as suggested by the yellow color of this compound.

The $P(1)O_4$ tetrahedron presents the usually observed geometry of monophosphate groups with four homogeneous P(1)−O distances, ranging from 1.530(4) to 1.545(4) Å (Table 3). The second tetrahedron $P(2)O_3(OH)$ is less regular, with two short distances corresponding to the two free apexes O(7) and O(8) (1.505(4) and 1.495(4) Å, respectively), one usual P(2)−O(5) distance of 1.536(4) Å, and one long bond with O(6) i.e., with the hydroxyl group (1.601(4) Å).

The Ba(1) cation is environed by 10 oxygen atoms forming a distorted bicapped cube (Figure 3a) with Ba(1)−O distances ranging from 2.680(4) to 3.107(4) Å (Table 3). The second barium cation Ba(2) is also in a 10-fold coordination, but the oxygen atoms delimit this time an irregular pentagonal prism with Ba(2)−O

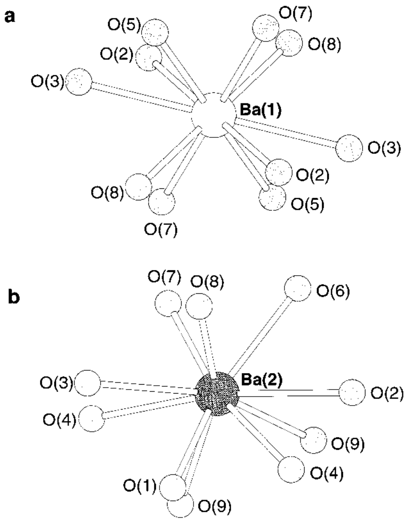

Figure 3. Environment of the barium cations: (a) Ba(1), (b) Ba(2).

distances ranging from 2.637(4) to 3.176(4) Å (Figure 3b, Table 3).

Concluding Remarks

The quantitative synthesis of the new uranyl monophosphate $Ba_3[UO_2(PO_4)(PO_3(OH))]_2 \cdot xH_2O$ shows that the Ba−P−O system is a very promising route for the research of crystallized phosphates loaded with hexavalent uranium. The presence in the structure of large amounts of barium is a very important trump for the use of such systems for radioactive uranium storage, owing to the great ability of barium to form matrixes resistant to radiation effects. This Ba−U−P−O is more interesting, as the temperature for the synthesis is very low (200 °C). Moreover, the formation of an anhydrous phase at higher temperature constitutes a second interesting direction for the research of new crystallized uranium-based barium phosphates.

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Supporting Information Available: Calculated and observed structure factors for $Ba_3[UO_2(PO_4)(PO_3(OH))]_2 \cdot xH_2O$ (12 pages). Ordering information is given on any current masthead page.

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