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Synthesis and Crystal Structure of Thorium Bis(hydrogenphosphate) Monohydrate

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Microcrystals of $Th(HPO_4)_2{\cdot}H_2O$ were hydrothermally obtained from a $Th(NO_3)_4-CO(NH_2)_2-H_3PO_3-H_2O$ system ($T = 180$ ºC). The structure [orthorhombic, *Pbca*, $a = 9.1968(2)$ Å, $b = 18.6382(2)$ Å, $c = 8.7871(2)$ Å], unlike α-$Zr(HPO_4)_2{\cdot}H_2O$-type layered compounds, consists of a three-dimensional framework with PO_4 tetrahedra coordinated to Th atoms. The water molecule is also coordinated to the Th atom and projected toward small channels running along the directions of the *a* and *c* axes. The $ThO_6O(w)$ environment could be described as a highly distorted pentagonal bipyramid.

Since 1969, the year in which Clearfield and Smith published the first structure of a metal(IV) bis(hydrogenphosphate) monohydrate, $Zr(HPO_4)_2{\cdot}H_2O$ (α-ZrP),[1,2] this family of materials has grown to include all metals of groups 4 and 14. The $M(HPO_4)_2{\cdot}H_2O$ (M = Ti, Zr, Hf, Ge, Sn, Pb) isostructural compounds (denoted as α-MP),[3–5] with a layered feature that shows a resemblance to clay minerals,[6] are interesting in many fields of application (ion exchange, intercalation, catalysis, and ion conduction).[7–11]

Recently, we reported the structural characterization of the first cerium(IV) phosphate with a P/Ce molar relationship equal to 2, $(NH_4)_2Ce(PO_4)_2{\cdot}H_2O$,[12] and our intention to search for both synthesis procedures and structural data from related compounds, in particular $M(HPO_4)_2{\cdot}H_2O$ (M = tetravalent inner transition metal).

In the field of the specific immobilization of radioelements such as actinides originating from the reprocessing of spent nuclear fuel, several phosphate matrixes have been extensively studied.[13–16] However, in spite of numerous efforts, the family of structurally characterized thorium phosphates is still small: α-ThP_2O_7, $Th_2O(PO_4)_2$, $Th(OH)PO_4$, α- and β-$Th_4(PO_4)_4P_2O_7$, $Th_4(PO_4)_4P_2O_7{\cdot}2H_2O$, and $Th_2(PO_4)_2(HPO_4){\cdot}H_2O$.[17–21] In addition, although interest concerning actinide(IV) hydrogenphosphates has existed for a long time, only amorphous or less crystallized solids with a variable degree of hydration, $M(HPO_4)_2{\cdot}nH_2O$ (M = Th, U, Pu),[22] have been described to date.

The synthesis of phosphorus(V) compounds starting from phosphorous acid is a barely explored route. However, it is known that this procedure is useful for the preparation of phases not accessible by conventional procedures.[19,23,24] It is clear that the kinetics of crystallization of the final product

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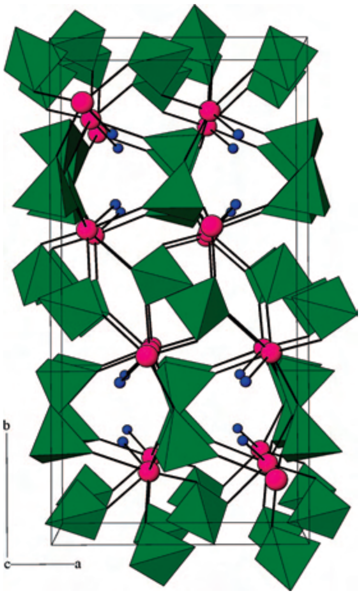

Figure 1. Representation of the structure of $Th(HPO_4)_2 \cdot H_2O$ along the *c* axis with the *b* axis vertical (PO_4, tetrahedra; Th, purple circles; O_W, blue circles).

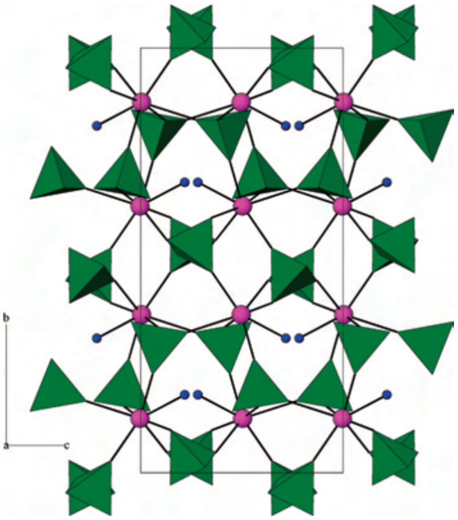

Figure 2. Representation of the structure of $Th(HPO_4)_2 \cdot H_2O$ along the *a* axis with the *b* axis vertical (PO_4, tetrahedra; Th, purple circles; O_W, blue circles).

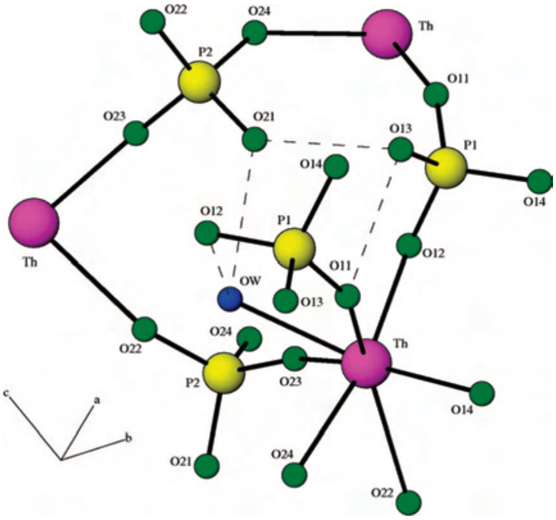

Figure 3. Representation of the environment around one Th atom showing the proposed hydrogen-bond scheme.

will depend on the phosphate concentration in solution. This concentration is a function of the capacity to oxidize phosphorus(III) under experimental conditions. In accordance with the premise, the reaction will be kinetically controlled, leading to products of both high purity and crystallinity.

In this study, microcrystals of $Th(HPO_4)_2 \cdot H_2O$ were hydrothermally obtained from a $Th(NO_3)_4-CO(NH_2)_2-H_3PO_3-H_2O$ system. The structure of this compound, the first reported inner-transition monohydrogenphosphate, was solved by synchrotron powder X-ray diffraction (XRD). Its orthorhombic structure was solved with the space group *Pbca* (No. 61) with the following final unit cell parameters: $a = 9.1968(2)$ Å, $b = 18.6382(2)$ Å, $c = 8.7871(2)$ Å, and $V = 1506(2)$ Å^3.

The $Th(HPO_4)_2 \cdot H_2O$ structure bears absolutely no resemblance to the α-ZrP-type materials. It consists of PO_4 tetrahedra coordinated to Th atoms to form a three-dimensional framework. Th atoms are located at four different planes inside the unit cell at $y = 0.128$, 0.372, 0.628, and 0.872, separated by approximately a quarter of the length of the *b* axis. These planes are joined alternatively by P1 and P2 phosphate groups. The link by P1 groups forms a dense layer, whereas the link by P2 groups forms small channels along the [001] (Figure 1) and [100] (Figure 2) directions. The Th atom is surrounded by seven O atoms in a distance range of 2.226(3)–2.487(3) Å, involving six monodentate phosphate groups and the water molecule, which is projected toward the small channels. This environment could be described as a highly distorted pentagonal bipyramid. Therefore, the Th atom in this compound is seven-coordinated, like in $Th_2(PO_4)_2(HPO_4) \cdot H_2O$, as opposed to the eight coordination in $Th_4(PO_4)_4P_2O_7$ or the rare octahedral coordination in cubic α-ThP_2O_7. The two phosphate groups are linked to three Th atoms. The atoms O13 and O21 do not belong to the coordination environment of Th atoms and have close contacts between them and with the water molecule. It is thus plausible that these atoms hold the H atoms of the HPO_4 groups. A possible hydrogen-bond scheme would be $O11 \cdots H-O13 \cdots H-O21 \cdots H-O_W-H \cdots O12$, forming with the O11−P1 and P1−O12 bonds isolated six-membered rings (Figure 3).

Each Th atom is linked to six P atoms, three P1 and three P2, through monodentate coordination (Figure 4). Each P atom is linked to three Th atoms. In the case of P1, two of the Th atoms are joined through two O−P1−O bridges, forming a dinuclear structural unit where the two thorium clusters are related by symmetry. Two of the hydrogen-bond contacts are between the water molecule O atom, hydroxyl O atoms, and other O atoms inside one thorium cluster. These intracluster contacts occur with the formation of five-membered rings with a high degree of planarity, in a

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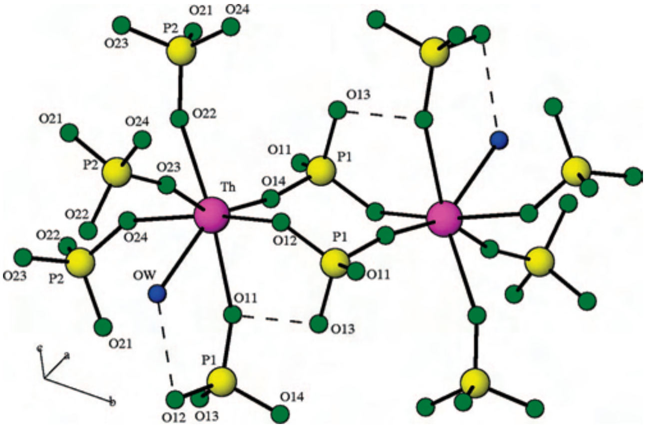

Figure 4. Representation of the environment around two symmetry-related Th atoms. Dashed lines represent hydrogen-bond contacts.

geometrical distribution also observed in other metal phosphates.[25]

The thermogravimetric and differential thermogravimetric (DTG) data show that the release of the water molecule takes place at $T > 110$ °C (DTG minima at 190 °C), causing structural collapse, with the formation of α-ThP_2O_7 in a single step ($\Delta H = 135 \pm 5$ kJ mol^{-1}).

In conclusion, given the potential applications of actinide phosphates in the field of radioelement immobilization, the structural characterization of the first inner-transition monohydrogenphosphate should encourage researchers to search for structural data from related compounds, in particular $M(HPO_4)_2{\cdot}nH_2O$ ($M = U$, Pu).

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Supporting Information Available: X-ray crystallographic data in CIF format and synthesis, experimental procedures (thermal analysis and powder XRD data), and details on the crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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