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# New Hydrothermal Synthesis and Structure of $Th_2(PO_4)_2(HPO_4)\cdot H_2O$: the First Structurally Characterized Thorium Hydrogenphosphate

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$Th_2(PO_4)_2(HPO_4)\cdot H_2O$ was synthesized under wet hydrothermal conditions starting from a mixture of $H_3PO_3$ and $Th(NO_3)_4\cdot 5H_2O$. The crystal structure was solved by powder X-ray diffraction data. The unit cell parameters are $a = 6.7023(8)$ Å, $b = 7.0150(8)$ Å, $c = 11.184(1)$ Å, $\beta = 107.242(4)°$, space group $P2_1$, and $Z = 2$. The structure consists of layers of both thorium atoms and $PO_4$ groups, alternating with a layer formed by $HPO_4$ entities and water molecules. By thermal treatment, this compound turns into $Th_4(PO_4)_4P_2O_7$, a ceramic already described in the field of the immobilization of tetravalent actinides.

## Introduction

In the field of the specific immobilization of radioelements such as actinides coming from the reprocessing of nuclear spent fuel, several phosphate matrixes such as britholites $Ca_9Nd(PO_4)_5(SiO_4)F_2$,[1] monazites $M^{III}PO_4$ and associated brabantites $N^{II}M^{IV}(PO_4)_2$ (M = Th, U, ...; N = Ca, Cd, Sr, Pb, ...),[2−5] sodium−zirconium phosphate $NaZr_2(PO_4)_3$ (NZP),[6] or thorium phosphate-diphosphate $Th_4(PO_4)_4P_2O_7$ (so-called TPD)[7] have been extensively studied. Indeed, phosphate materials and minerals are usually very resistant to aqueous alteration and very low-soluble. In this way, we can report the good chemical durability of monazites[8] or TPD[9−11] during leaching tests and the presence of large amounts of thorium and uranium in phosphate ores containing monazites, brabantites, or apatites.[12,13] Moreover, phosphate matrixes are usually resistant to radiation damages since associated minerals are rarely observed in the metamict form.[2,14]

TPD has been prepared from both dry and wet chemistry methods.[7] The first way consists of a high-temperature reaction between $ThO_2$ and $NH_4(H_2PO_4)$, while the second is based on a mixture of concentrated solutions of both thorium nitrate (or chloride) and phosphoric acid. The mixture is heated to get a dry residue that is transformed

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into TPD after heating at high temperature. Later, the solid obtained by precipitation from thorium salts and phosphoric acid was characterized as an amorphous phase, $Th_2(PO_4)_2(HPO_4)\cdot nH_2O$ ($n = 3-7$).[15] More recently, the monohydrated compound, $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ (TPHPH), which also appears as a precursor of TPD, was obtained from a mixture of thorium nitrate and phosphoric acid solutions in hydrothermal conditions.[16]

TPD was first prepared for the efficient and specific conditioning of large amounts of tetravalent actinides,[17−19] especially $^{239}Pu$ ($T_{1/2} = 2.5 \times 10^4$ yr) and $^{237}Np$ ($T_{1/2} = 2.1 \times 10^6$ yr) for the long-term storage. These radionuclides could be incorporated during the “traditional” synthesis of TPD (its efficient sintering being performed through a two-step procedure involving a uniaxial pressing at room temperature and then a heating treatment between 1050 °C and 1250 °C).[20] An interesting alternative is that the radionuclides could be precipitated in the structure of the precursor, prior to its thermal conversion into final TPD by heating at 1150−1250 °C. One of the main advantages of this new way concerns the significant improvement of the homogeneity of the final solid solutions prepared, especially considering the repartition of the cations (e.g., thorium and uranium) in the final crystallized phase.[21]

In this context, as a potential candidate for practical applications, it is necessary for a detailed knowledge of the properties of $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ (TPHPH) that only can be explained if the structural features are known. Up to now, the efforts to solve the structure of this compound had been fruitless. We report here a new hydrothermal procedure for the synthesis of TPHPH and its structural determination from powder diffraction data.

## Experimental Section

**Sample Preparation and Analytical Procedures.** Hydrothermal synthesis of $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ was carried out in a stainless steel Teflon-lined vessel (100 mL) under autogenous pressure. 2.76 g of $Th(NO_3)_4\cdot 5H_2O$ (solid, Merck), 1.64 g of $H_3PO_3$ (solid, Merck), and 15 mL of distilled water were mixed, and the autoclave was sealed and then heated at 190 °C for 7 days. The obtained solid was filtered, washed with an excess of distilled water, and then dried in air at room temperature. The phosphorus and thorium contents were determined by ICP-MS analysis (Finnigan, Element model) after dissolving 0.5 g of sample in HF(aq). The results of elementary analysis: (P: 12.1 wt %, Th: 59.7 wt %) were in good agreement with that calculated for $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ (P: 12.11 wt %, Th: 60.42 wt %). Thermogravimetric analysis (Mettler TA4000-TG50) was carried out under nitrogen flow with a rate of 10 °C min$^{-1}$ (Figure 1). The total weight loss was equal to 3.6% up to 1000 °C while the final product was identified as TPD. This result agrees well with the loss of 1.5 water molecules per unit formula (calcd 3.51%). The total weight loss occurs below 400 °C (Figure 1) in two overlapped steps, with maximum dehydration speeds at 250 °C and 300 °C (minima on the DTG curve). The DSC curve (Mettler TA4000-DSC30, $N_2$-atmosphere, heating rate of 10 °C min$^{-1}$) shows also two individual processes.

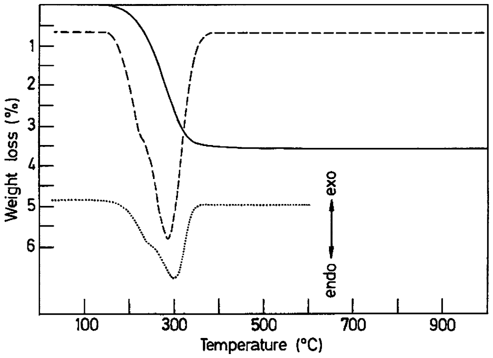

**Figure 1.** TG (—), DTG (---) and DSC (····) results obtained for TPHPH.

Infrared absorption spectra (Figure 2) were recorded on a Perkin-Elmer 1720-X FT spectrophotometer by the KBr pellet technique. SEM micrographs (recorded with a JEOL JSM-6100 electron microscope operating at 20 kV) reveal the platelike morphology of the grains with an irregular form and a thickness smaller than 1 $\mu$m.

**X-ray Diffraction Study.** An XRD powder pattern of $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ was collected on a Seifert XRD3000 X-ray diffractometer, belonging to the SCT’s facilities of the University of Oviedo, operating in Bragg−Brentano $\theta$-$\theta$ geometry at 50 kV and 40 mA and using graphite monochromated Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å). The data were collected at room temperature over the angular $2\theta$ range 7−107° with a step of 0.02° and a counting time of 10 s on a sample gently ground in an agate mortar.

The pattern was indexed in the monoclinic system with lattice parameters $a = 6.710(4)$ Å, $b = 7.024(2)$ Å, $c = 11.207(8)$ Å, and $\beta = 107.38(7)°$ and figures of merit: $M_{20} = 46$, $F_{20} = 63(0.006,53)$ using the program TREOR.[22] The observed reflections showed only systematic absences of the type $0k0$, $k = 2n + 1$, indicating the space group was either $P2_1$ or $P2_1/m$. A pattern matching was carried out with the FULLPROF program[23] with an interpolated background and refining the zero shift, peak shape parameters for the pseudo-Voigt function, and cell parameters. The structure was determined ab initio using a direct space search approach with the program FOX.[24] The procedure was started without any structural previous information apart from the unit cell, space group, and composition from a configuration composed by two independent thorium atoms and three idealized phosphate groups in random positions and orientations. The use of rigid polyhedra greatly reduces the number of involved variables. For the background and profile parameters, we took, respectively, the values previously used and refined in the pattern matching. A solution was found in the space group $P2_1$. Profile refinement was carried out by the Rietveld method. After refinement of profile parameters, a difference Fourier

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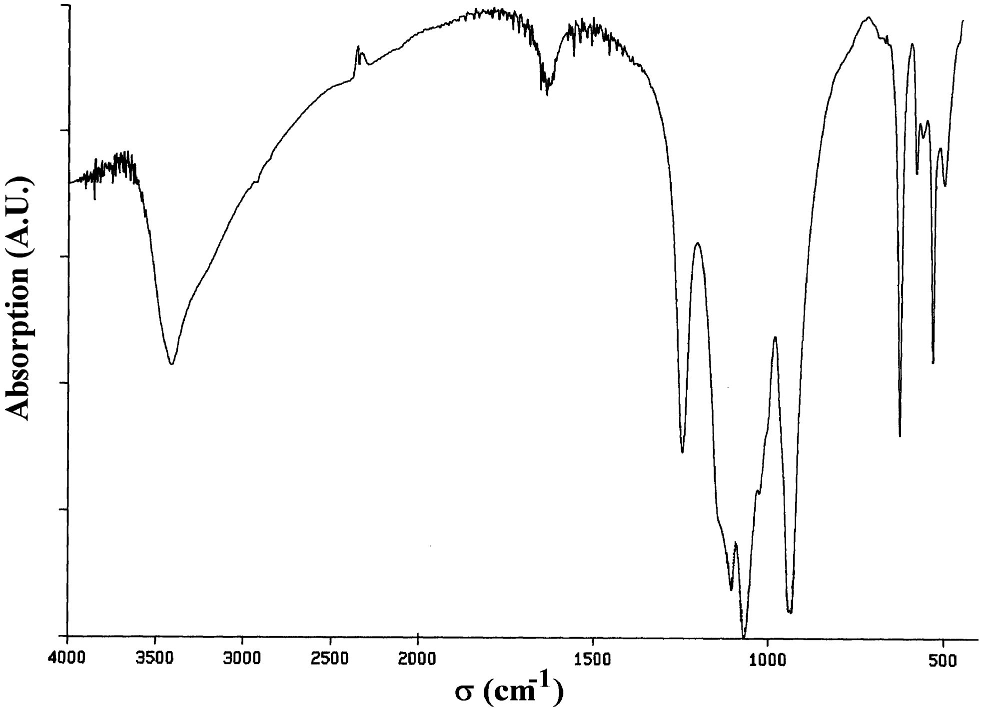

**Figure 2.** Absorption infrared spectra of TPHPH.

synthesis was made using SXELXL97[25] and observed $F^2$ from refinement, showing the possible position of the oxygen of a water molecule that was included in the atomic set. A symmetry check was performed on the atomic coordinates to verify the absence of a center of symmetry and confirm the space group choice.

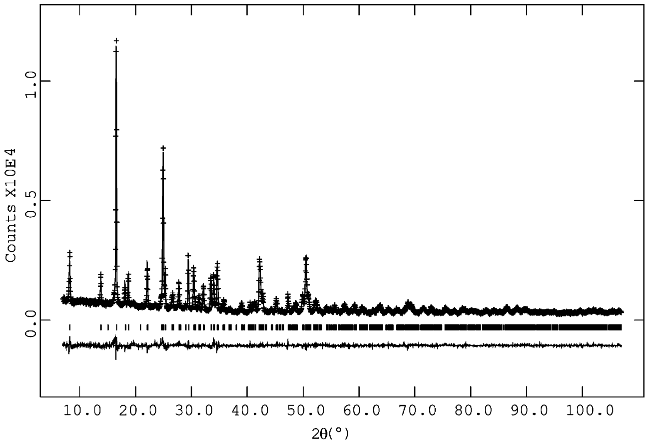

**Figure 3.** X-ray diffraction powder pattern of TPHPH. Observed (+), calculated (line), and difference (below) profiles are plotted on the same scale. Bragg peaks are indicated by tick marks.

The final structure refinement was carried out with the program GSAS.[26] The structural refinement was hindered by the presence of the strong scattering of thorium atoms. For that reason, rigid body constraints were invoked for PO$_4$ groups assuming an ideal tetrahedral geometry with bond distance 1.53 Å. Although diverse temperature factor schemes were tried, these lead to some meaningless values and the changes in the atomic coordinates were negligible, probably because in this case the accuracy of the atomic positions is largely determined by the use of rigid body constraints. Then, all atoms were refined isotropically with a common temperature factor, $U = 0.0278(11)$ Å$^2$. Soft constraints were needed for the water oxygen atom to avoid too short contacts with other oxygen atoms. A preferred orientation was introduced through the spherical-harmonics function[27] implemented in GSAS. The final Rietveld plot is shown in Figure 3. Crystallographic parameters are collected in Table 1. Final atomic coordinates are reported in Table 2, with selected interatomic distances in Table 3. The asymmetric unit consists of two independent thorium atoms, three phosphate groups, and one oxygen atom belonging to a water molecule.

## Results and Discussion

The synthesis of phosphorus(V) compounds starting from phosphorous acid is a little explored route. However, it is known that this procedure is useful for the preparation of nonaccessible phases by conventional procedures.[28] It is clear that the kinetics of crystallization of the phosphate will depend on the phosphate concentration in solution. This concentration will be dependent on the capacity for oxidizing the phosphorus(III) in the experimental conditions. With these premises, the reaction will be kinetically controlled, leading to products of both high purity and crystallinity.

As described in the Experimental Section, TPHPH was obtained starting from H$_3$PO$_3$ in aqueous medium. This new chemical way of synthesis provided an appropriate material to approach its structural resolution by means of X-ray powder diffraction methods.

The infrared absorption spectrum (Figure 2) exhibited both O−H stretching and H−O−H bending vibrations.[29,30] The

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**Table 1.** Crystallographic Parameters for the Powder X-ray Diffraction Study of TPHPH

| | |
|---|---|
| empirical formula | $Th_2P_3H_3O_{13}$ |
| color | white |
| $M_r$ (g mol$^{-1}$) | 768 |
| cryst. system | monoclinic |
| wavelength (Å) | 1.5418 |
| $a$ (Å) | 6.7023(8) |
| $b$ (Å) | 7.0150(8) |
| $c$ (Å) | 11.184(1) |
| $\beta$ (°) | 107.242(4) |
| Z | 2 |
| space group | $P$21 (N° 4) |
| $2\theta$ range (°) | 7−107 |
| step (°) | 0.02 |
| count/step (s/°) | 10 |
| parameters | 65 |
| $R_p$ | 0.054 |
| $R_{wp}$ | 0.068 |
| $R_{exp}$ | 0.043 |
| $R(F^2)$ | 0.079 |

**Table 2.** Fractional Atomic Coordinates for TPHPH

| atom | x | y | z |
|---|---|---|---|
| Th1 | 0.2880(9) | 0.6657 | 0.2806(4) |
| Th2 | 0.0054(9) | 0.667(5) | 0.7184(4) |
| P1 | 0.497(5) | 0.669(8) | 0.6332(17) |
| P2 | 0.825(3) | 0.457(5) | 0.9811(18) |
| P3 | 0.878(4) | 0.665(18) | 0.3584(19) |
| O11 | 0.302(6) | 0.711(12) | 0.673(3) |
| O12 | 0.665(8) | 0.817(9) | 0.691(6) |
| O13 | 0.442(7) | 0.678(14) | 0.4904(18) |
| O14 | 0.579(9) | 0.470(8) | 0.678(6) |
| O21 | 0.008(4) | 0.393(5) | 0.0914(24) |
| O22 | 0.714(3) | 0.625(5) | 0.0215(17) |
| O23 | 0.671(4) | 0.292(5) | 0.9386(20) |
| O24 | 0.905(4) | 0.519(5) | 0.8727(22) |
| O31 | 0.892(7) | 0.67(3) | 0.4974(21) |
| O32 | 0.991(24) | 0.838(19) | 0.326(11) |
| O33 | 0.649(4) | 0.67(3) | 0.279(4) |
| O34 | 0.980(24) | 0.482(18) | 0.331(11) |
| OW | 0.679(4) | 0.992(6) | 0.0889(29) |

**Table 3.** Interatomic Distances (Å) around Thorium Atoms and Selected Contacts

| | | | |
|---|---|---|---|
| Th1−O12 | 2.47(6) | Th2−O11 | 2.21(4) |
| Th1−O13 | 2.268(24) | Th2−O12 | 2.44(6) |
| Th1−O14 | 2.31(5) | Th2−O21 | 2.676(28) |
| Th1−O23 | 2.695(24) | Th2−O24 | 2.277(23) |
| Th1−O32 | 2.50(17) | Th2−O31 | 2.361(23) |
| Th1−O33 | 2.42(3) | Th2−O32 | 2.36(12) |
| Th1−O34 | 2.63(17) | Th2−O34 | 2.29(12) |
| | | Th2−OW | 2.813(25) |
| O12···O21 | 2.80(5) | O21···O34 | 2.81(12) |
| O23···O33 | 2.86(8) | O24···O32 | 2.82(11) |
| OW···O22 | 2.716(15) | OW···O22* | 2.719(15) |
| OW···O23 | 2.68(3) | OW···O23* | 2.677(15) |
| OW···O24 | 2.695(15) | | |

large band pointed at 3410 cm$^{-1}$ was assigned to all O−H stretching vibrations, while the band located at 1636 cm$^{-1}$ corresponds to the bending mode of water. Considering several studies regarding phosphate compounds,[31−33] the vibrations of the P−O bonds are observed from 500 to 630 cm$^{-1}$ ($\delta_{AS}$), from 920 to 980 cm$^{-1}$ ($\nu_S$), and from about 1000 to 1160 cm$^{-1}$ ($\nu_{AS}$) in the infrared absorption spectra of TPHPH. Moreover, the band corresponding to the symmetric stretching mode of the P−O−P bridge, $\nu_S$(P−O−P) (between 700 and 750 cm$^{-1}$), was not observed in the IR spectra excluding the presence of $P_2O_7$ entities in the precipitate. As already described for several hydrogenphosphate hydrated compounds, the observation of one shoulder at about 3200 cm$^{-1}$, in the IR spectra, can be associated to the (P)−O−H stretching modes.[29] Moreover, the intense band located near 1250 cm$^{-1}$ may be assigned to the stretching mode in the plane of the P−O−H bonds[29] or to the presence of water molecules adsorbed on phosphate layers.[34] The deformation mode of P−O−H bonds could be assigned to the band located between 910 and 940 cm$^{-1}$. From these results, the spectroscopic observations confirmed the simultaneous presence of $HPO_4$ and $PO_4$ groups in the solid. For the discussion of IR assignment, see also ref 16.

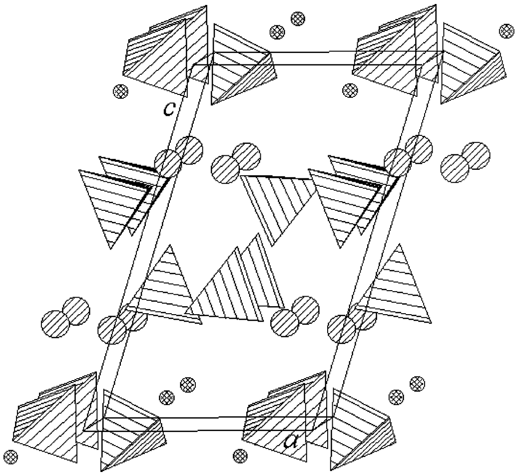

**Figure 4.** Representation of the structure of TPHPH along the *b* axis with the *c* axis vertical ($PO_4$, tetrahedra; Th, big lined circles; OW, small doubly lined circles).

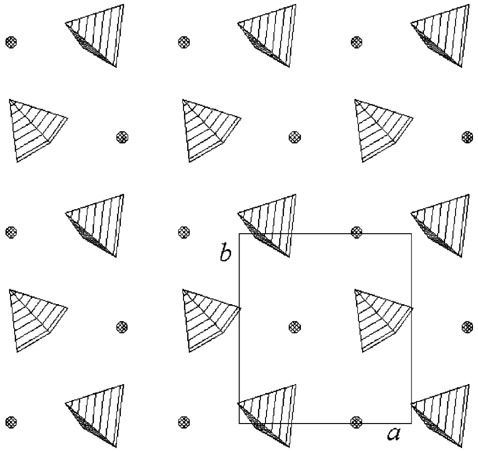

**Figure 5.** Perpendicular view of one hydrogenphosphate−water layer of TPHPH (see Figure 4 for the meaning of symbols).

The structure of $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ (Figure 4) can be described as layers including both thorium atoms and two $PO_4$ groups, alternating with a layer formed by a third set of $PO_4$ groups with the water molecules filling the holes left in the layer (see Figure 5). As discussed below, this phosphate

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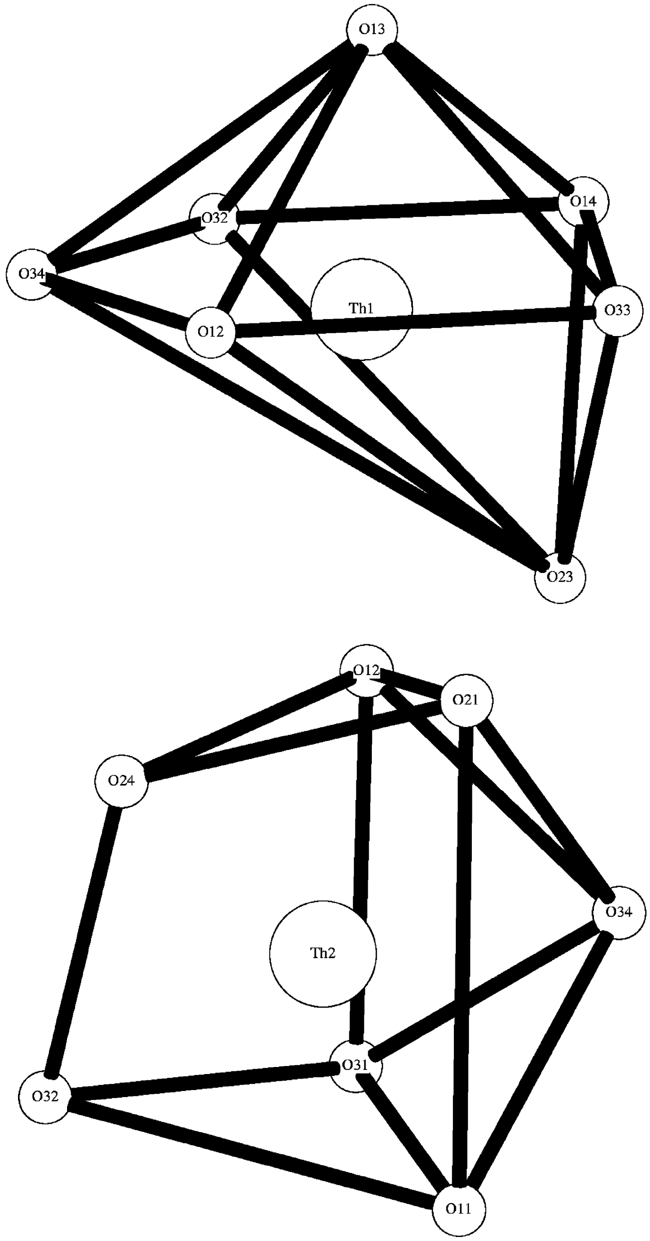

**Figure 6.** Representation of the Th1 (a) and Th2 (b) polyhedra.

group could be identified to the hydrogenphosphate one ($HPO_4$), and then this layer would be held by a strong hydrogen bond network between $HPO_4$ entities and water molecules. The geometry of isolated phosphate groups in inorganic monophosphates is quite regular, although obviously there are slight differences when distances and angles can be obtained with precision. Unfortunately, in this case because of the presence of heavy thorium atoms, we were obliged to use rigid body constraints for $PO_4$ groups. The quality of the powder diffraction refinement (low $R_{wp}$ and small difference pattern) indicates that the structure is fully described by the proposed model. Hydrogen atoms could not be located from the available diffraction data and, on the other hand, bond-valence sum rules cannot be used here because all the distances P−O are constrained to the ideal value 1.53 Å.

The Th1 atom is surrounded by seven oxygen atoms in a distance range 2.268(24)−2.695(24) Å, involving five monodentate and one bidentate phosphate groups. This environment could be described as a highly distorted pentagonal bipyramid (Figure 6a). The Th2 atom is also surrounded by seven oxygen atoms in a distance range 2.21(4)−2.676(28) Å involving seven monodentate phosphate groups. This environment could be described as a monocapped trigonal prism (Figure 6b). The next closest atom is an oxygen belonging to a water molecule at 2.813(25) Å. Therefore, the coordination of both thorium atoms in this compound is seven as opposed to the more usual eight coordination in $Th_4(PO_4)_4P_2O_7$ or the rare octahedral coordination in cubic $ThP_2O_7$.[35] Th1 and Th2 polyhedra, through sharing one edge (O12 and O34) and one vertex (O32), form chains running along the direction [010]. In the $An_2O(PO_4)_2$ family, the structure contains infinite zigzag chains of double edge-sharing $AnO_7$ polyhedra where the metal atom adopts a pentagonal bipyramidal arrangement as observed in many uranium compounds.[36]

The phosphate $(PO_4)1$ is surrounded by five thorium atoms, three Th1 and two Th2, acting always as a monodentate group. The O12 atom acts as a bridge between one Th1 and one Th2 atoms. The phosphate $(PO_4)3$ is surrounded by five thorium atoms, two Th1 and three Th2, and acts as a bidentate ligand for one Th1 atom with the two oxygen atoms involved (O32 and O34) acting also as bridges between the Th1 and two Th2 atoms. The hydrogenphosphate $(PO_4)2$ is surrounded by three thorium atoms, one Th1 and two Th2, acting always as a monodentate group. The oxygen atom O22 does not belong to the coordination environment of thorium atoms and it is close to the oxygen of water molecule. Then, it is plausible that this atom holds the hydrogen atom of the $HPO_4$ group.

## Conclusions

In recent years, TPD was evidenced to be well appropriated for the storage of large quantities of tetravalent actinides because of the formation of solid solutions with large amounts of tetravalent actinides such as uranium (IV), neptunium (IV), and plutonium (IV) by replacement of thorium in the structure.[17−19] Moreover, the high durability of the ceramics during leaching tests led to very low normalized dissolution rates even in aggressive media.[9,10] Since TPD-type compounds could be obtained by thermal treatment of TPHPH-type materials,[15] the knowledge of the structural features of these solids are decisive for the understanding of their behavior in real systems.

To the best of our knowledge, TPHPH is the first structurally characterized thorium hydrogenphosphate. This compound, together with α-$ThP_2O_7$, $Th_2(PO_4)(P_3O_{10})$,[37] $Th_2O(PO_4)_2$,[16] and $Th_4(PO_4)_4P_2O_7$ (TPD), constitute the small family of known thorium(IV) phosphates. We are working

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on the synthesis and structural characterization of new members of this interesting compound group. The presence in TPHPH of $HPO_4$ groups joined by hydrogen bonds to water molecules forming layers suggest that, in suitable conditions, ion exchange process ($H^+/M^{n+}$) will be possible for small $M^{n+}$ mono- or divalent cations. This fact will be relevant in the formation of this structural type in complex reaction mixtures. Therefore, the synthesis and structural characterization of new metal TPHPH substituted phases deserve to be the subject of future studies.

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