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Article

Phosphorous Acid and Urea: Valuable Sources of Phosphorus and Nitrogen in the Hydrothermal Synthesis of Ammonium-Thorium Phosphates

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Microcrystals of the first ammonium-thorium phosphates, $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ (tetragonal, $I4_1/amd$, $a = 7.0192(4)$ Å, $c = 17.9403(8)$ Å) and $NH_4Th_2(PO_4)_3$ (monoclinic, $C2/c$, $a = 17.880(6)$ Å, $b = 6.906(1)$ Å, $c = 8.152(2)$ Å, $\beta = 104.39(2)°$) were hydrothermally obtained from a $Th(NO_3)_4$-$CO(NH_2)_2$-H_3PO_3-H_2O system ($T = 180$ °C). In both cases, the structure consists of a three-dimensional framework with PO_4 tetrahedra coordinated to Th atoms (ThO_n polyhedra, where $n = 8$ or 9, for the tetragonal or monoclinic phase, respectively). The ammonium ions (and water molecules) are located in the tunnels.

Introduction

The immobilization of radionuclides in an underground repository can be considered as one of the options for the management of long-lived and highly radioactive radionuclides.[1,2] In this field, our research group recently reported both the synthesis and structural characterization of the first inner-transition monohydrogenphosphate, $Th(HPO_4)_2 \cdot H_2O$,[3] following an experimental procedure (hydrothermal synthesis with H_3PO_3 as the source of phosphorus) similar to that previously used by us in the preparation of well crystallized $Th_2(PO_4)_2(HPO_4) \cdot H_2O$,[4] which is the precursor (by thermal treatment) of β-$Th_4(PO_4)_4P_2O_7$:[5,6] between 180 and 220 °C, $Th_2(PO_4)_2(HPO_4) \cdot H_2O$ dehydrates leading to the anhydrous thorium phosphate-hydrogenphosphate, that progressively transforms above 220 °C into the low-temperature form of the thorium phosphate-diphosphate, α-$Th_4(PO_4)_4P_2O_7$, and this compound changes into the high-temperature form, β-$Th_4(PO_4)_4P_2O_7$, by heating above 950 °C. This last material is a promising ceramic for the specific immobilization of tetravalent actinides, as it allows the incorporation of large amounts of uranium, neptunium, or plutonium by substitution of thorium in its crystal structure,[7,8] and is strongly resistant to aqueous alteration and to radiation damage.[9–13]

The synthesis of phosphorus(V) compounds starting from phosphorous acid is an unusual (although useful) procedure for preparing phases not accessible by conventional methods.[14,15] Similarly, urea is not a common source of ammonia, although this reagent has demonstrated its effectiveness in the synthesis of iron(III) phosphates,[16] including exotic phases such as $Fe(NH_3)_2PO_4$.[17]

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Table 1. Analytical Data and Weight Loss at 1000 °C (w.l.) for the New Compounds (Mass %)

	$(NH_4)_2Th(PO_4)_2 \cdot H_2O$		$NH_4Th_2(PO_4)_3$	
	experimental	calculated	experimental	calculated
% Th	48.0	48.74	59.8	60.49
% P	12.9	13.02	12.0	12.12
% N	5.8	5.88	1.7	1.82
% w.l.	15.0	14.71	3.5	3.39

In this research study of the hydrothermal reactions in the $Th(NO_3)_4$-$CO(NH_2)_2$-H_3PO_3-H_2O system, the formation of several different thorium(IV) phosphate products is reached.

Experimental Section

Sample Preparation and Analytical Procedures. The syntheses were performed under hydrothermal conditions in a stainless steel Teflon-lined vessel (100 mL) under autogenous pressure. Weighed amounts of the reagents ($Th(NO_3)_4 \cdot 5H_2O$, H_3PO_3, $(NH_2)_2CO$, all Merck solids) were mixed with 15 mL of distilled water. The autoclaves were sealed and then heated to 180 °C for 10 days. The products thus obtained were filtered, washed with an excess of distilled water, and then dried in air at room temperature. In addition of three previously described thorium(IV) phosphates, two novel compounds were isolated and later on characterized. Phosphorus and thorium contents were determined by ICP-MS analysis (Finnigan, Element model) after dissolving 0.5 g of the sample in HF(aq). The nitrogen content was determined on a C−H−N Perkin-Elmer model 2400B elemental analyzer. A Mettler-Toledo TA4000 was used for the thermal analyses under a dynamic nitrogen atmosphere (50 mL/min) at a heating rate of 10 °C/min. The analytical data were in good agreement with that calculated for $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ and $(NH_4)Th_2(PO_4)_3$ (see Table 1). For $(NH_4)_2Th(PO_4)_2 \cdot H_2O$, the TG and DTG data (Figure 1a) show that the top speed in the release of the water takes place at about 120 °C. In a later step (DTG minimum at 315 °C), the anhydrous compound is transformed into α-ThP_2O_7. $NH_4Th_2(PO_4)_3$ has a much higher thermal stability, and it only decomposes at $T > 700$ °C (DTG minimum at 880 °C), forming β-$Th_4(PO_4)_4(P_2O_7)$ as the final product (Figure 1b).

X-ray Diffraction Study. X-ray powder diffraction patterns of $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ and $(NH_4)Th_2(PO_4)_3$ were recorded at Oviedo University SCT facilities using a Seifert XRD3000 operating in Bragg−Brentano θ-θ geometry at 50 kV and 40 mA with graphite monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). The samples were gently ground in an agate mortar and size-loaded to minimize the preferred orientation. The patterns were indexed using the program TREOR.[18] Both structures were refined by the Rietveld method using the GSAS program[19] including a preferred orientation correction using a spherical-harmonics function.[20]

The $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ pattern was indexed in the tetragonal system with lattice parameters, $a = 7.0192(4)$ Å, $c = 17.9403(8)$ Å, and figures of merit: $M_{20} = 39$, $F_{20} = 50$ (0.007, 61). Systematic absences were consistent with the space group $I4_1/amd$. The crystal structure was refined starting from the isostructural compound $(NH_4)_2Ce(PO_4)_2 \cdot H_2O$.[21] As in the parent structure, the water molecule could not be located by difference Fourier synthesis in a unique site but rather seemed to be severely disordered around the ideal special position 0, 1/4, 7/8. The structure refinement including this position led to a very high displacement parameter for the oxygen of the water molecule. The water molecule was accordingly omitted from the refinement. All atoms were refined isotropically with a common temperature factor, $U = 0.0132(5)$ Å^2.

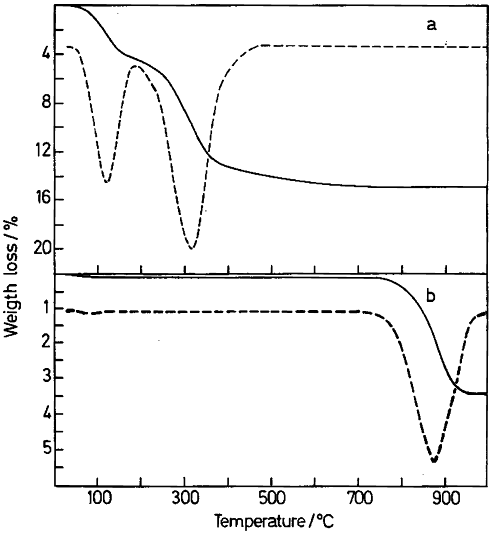

Figure 1. TG (solid line) and DTG (dashed line) data for (a) $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ and (b) $NH_4Th_2(PO_4)_3$.

The $NH_4Th_2(PO_4)_3$ pattern was indexed in the monoclinic system with lattice parameters, $a = 17.880(6)$ Å, $b = 6.906(1)$ Å, $c = 8.152(2)$ Å, $\beta = 104.39(2)°$, and figures of merit: $M_{20} = 19$, $F_{20} = 28$ (0.008, 88). Systematic absences were consistent with the space groups $C2/c$ and Cc. Successful refinement was carried out in $C2/c$. The crystal structure was refined starting from the isostructural compound $KTh_2(PO_4)_3$.[22] The structural refinement was hindered by the presence of the strong scattering of thorium atoms. For this reason, rigid-body constraints were invoked for PO_4 groups assuming an ideal tetrahedral geometry with bond distance 1.53 Å. All atoms were refined isotropically with a common temperature factor, $U = 0.0104(5)$ Å^2.

The final Rietveld plots are shown in Figure 2. Crystallographic parameters are collected in Table 2. Final atomic coordinates are reported as Supporting Information, with selected interatomic distances in Table 3.

Results and Discussion

In this research study of the hydrothermal reactions in the $Th(NO_3)_4$-$CO(NH_2)_2$-H_3PO_3-H_2O system, the formation of several different thorium(IV) phosphate products was found to depend both on the molar ratio of thorium- and phosphorus-containing reagents in the reaction mixture and on the acidity of the solution. Regulation of the acidity of the reaction system was achieved by adding different amounts of urea, which decomposes gradually with the release of NH_3(aq).

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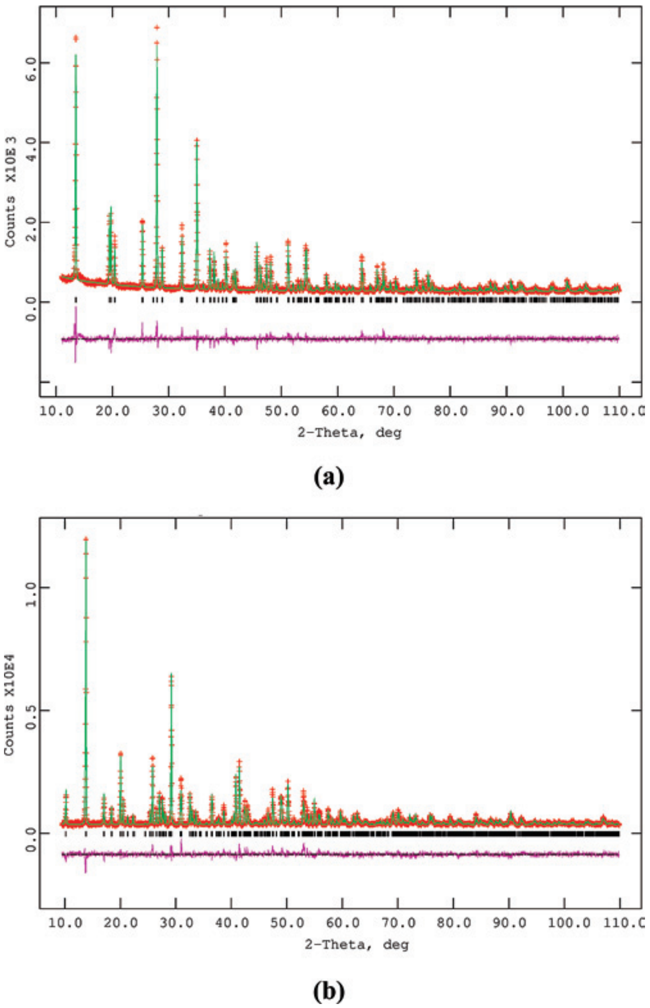

Figure 2. X-ray diffraction powder patterns of (a) $(NH_4)_2Th(PO_4)_2\cdot H_2O$ and (b) $NH_4Th_2(PO_4)_3$. Observed (+), calculated (line) and difference (below) profiles are plotted on the same scale. Bragg peaks are indicated by tick marks.

Table 2. Crystallographic Parameters for the New Compounds

	$(NH_4)_2Th(PO_4)_2\cdot H_2O$	$NH_4Th_2(PO_4)_3$
empirical formula	$ThP_2H_{10}O_9N_2$	$Th_2P_3H_4O_{12}N$
M_r	476.07	767.02
cryst. system	tetragonal	monoclinic
a (Å)	7.0192(4)	17.7238(5)
b (Å)		6.90676(12)
c (Å)	17.9403(8)	8.15603(32)
β (°)		102.1047(26)
Z	4	4
space group	$I4_1/amd$	$C2/c$
2θ range (°)	9−110	9−110
step (°)	0.02	0.02
count/step (s/°)	10	10
parameters	31	45
R_p	0.061	0.069
R_{wp}	0.079	0.088
R_{exp}	0.050	0.045
$R(F^2)$	0.14	0.19
χ	1.60	1.97

Figure 3 shows the ranges of concentration used for the preparation of individual crystalline phases. $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ is obtained in the absence of urea (when the P/Th molar ratio is higher than 1.5), as previously described.[4] However, $Th(OH)PO_4$ is formed as the sole product at lower P/Th molar ratios (<1.5).[23] Although a thorium(IV) hydrogenphosphate previously described, $Th(HPO_4)_2\cdot H_2O$,[3] is formed (in presence of urea) at low concentrations of phosphorous acid, when the P/Th molar ratio is higher than 4 the addition of urea to the reaction system leads to the formation of the two novel compounds, $(NH_4)_2Th(PO_4)_2\cdot H_2O$ and $NH_4Th_2(PO_4)_3$, as a function of the urea concentration in the reaction bulk. The structure of these compounds, the first reported ammonium-thorium phosphates, was solved by powder X-ray diffraction.

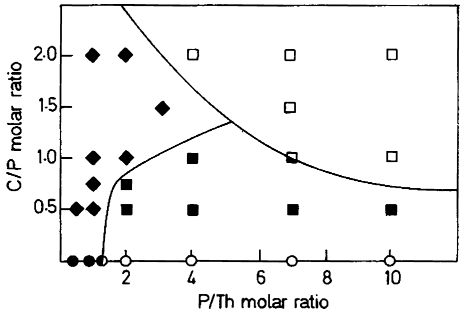

Figure 3. Phase diagram for the formation of thorium(IV) phosphates by reaction of $Th(NO_3)_4$(aq) and H_3PO_3(aq) in the presence of urea (T = 180 °C): $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ (○), $Th(OH)PO_4$ (●), $Th(HPO_4)_2\cdot H_2O$ (◆), $(NH_4)_2Th(PO_4)_2\cdot H_2O$ (□), and $NH_4Th_2(PO_4)_3$ (■).

Table 3. Selected Interatomic Distances (Å) for the New Compounds

	$(NH_4)_2Th(PO_4)_2\cdot H_2O$		
Th−O1 (x4)	2.417(12)	Th−O2 (x4)	2.558(9)
P−O1 (x2)	1.413(10)	P−O2 (x2)	1.521(11)
$N\cdots N^a$	2.80(8)	$N\cdots O2^{b,c}$	2.683(26)
$N\cdots O2^{d,e}$	3.115(28)		
	$NH_4Th_2(PO_4)_3{}^f$		
Th−O11	2.412(15)	Th−O12	2.743(23)
$Th-O12^g$	2.611(17)	Th−O13	2.772(27)
$Th-O13^h$	2.378(15)	Th−O14	2.238(15)
Th−O21	2.442(16)	$Th-O21^h$	2.796(28)
Th−O22	2.439(24)		
$N\cdots O14$ (x2)	2.855(18)	$N\cdots O21$ (x2)	2.88(4)
$N\cdots O22$ (x2)	2.83(4)		

[a] $-x + 2, y, z$. [b] $-y + 7/4, -x + 3/4, -z + 5/4$. [c] $y + 1/4, x + 3/4, -z + 5/4$. [d] $y - 1/4, -x + 3/4, z + 1/4$. [e] $-y + 5/4, x + 3/4, z + 1/4$. [f] P−O phosphate distances fixed at 1.53 Å. [g] $-x + 1/2, -y + 1/2, -z$. [h] $x, -y, z - 1/2$.

The structure obtained for $(NH_4)_2Th(PO_4)_2\cdot H_2O$ (Figure 4) is similar to that of the cerium analogue $(NH_4)_2Ce(PO_4)_2\cdot H_2O$.[21] It consists of ThO_8 distorted dodecahedra and PO_4 tetrahedra joined together to form a three-dimensional framework. This framework possesses small four-sided and larger six-sided tunnels running along equivalent [1 0 0] and [0 1 0] directions and interconnected with additional channels along [−1 1 1] and symmetry equivalent directions. In the cerium compound, this three-dimensional tunnel network leads to a substantial ionic conductivity.

The structure of $NH_4Th_2(PO_4)_3$ (Figure 5) is similar to that of its alkaline analogues $M^IM^{IV}_2(PO_4)_3$ (M^I = Li, Na, K, Rb, Cs; M^{IV} = Th, U, Np, Pu). It is built from PO_4 monophosphate groups and ThO_9 polyhedra sharing their apexes and their edges, thereby forming a three-dimensional framework. This is a different structure to that adopted by the $NaZr_2(PO_4)_3$ structural family (NASICON type), in which

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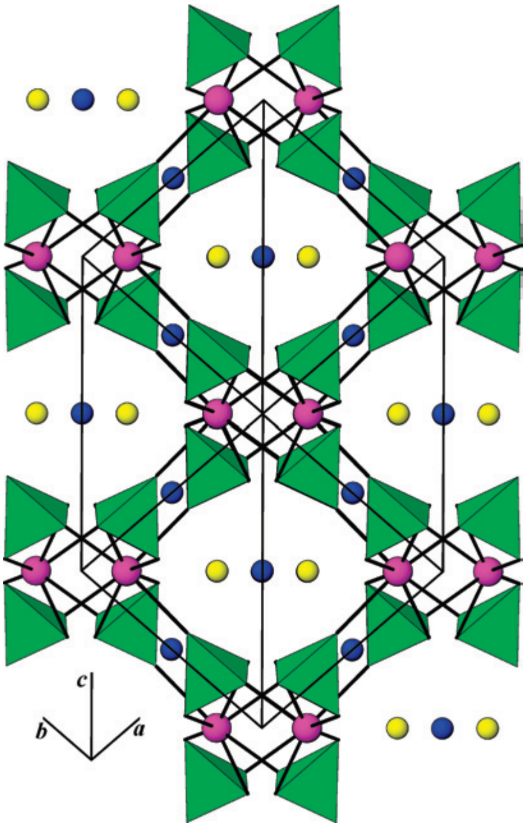

Figure 4. Representation of the structure of $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ along [1 1 −1] (PO_4, tetrahedral; Th, purple circles; N, blue circles; O_w, yellow circles).

the transition metal is hexacoordinated.[24,25] The ammonium ions are located in the tunnels running along *c* located on the 2-fold axis, as observed in $KTh_2(PO_4)_3$.[22] Splitting of the cationic site was observed in the structures of $KU_2(PO_4)_3$[26] and $NaTh_2(PO_4)_3$.[27]

Conclusions

In this paper, by using a very simple experimental strategy, we report the synthesis of the first structurally described ammonium-thorium phosphates, $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ and $NH_4Th_2(PO_4)_3$. In both cases, the structure (related with those of $(NH_4)_2Ce(PO_4)_2 \cdot H_2O$ and $M^ITh_2(PO_4)_3$ (M^I = Li, Na, K, Rb, Cs, Ag, Tl) compounds, respectively) consists of a three-dimensional framework with PO_4 tetrahedra coordinated to Th atoms (ThO_n polyhedra, where $n = 8$ or 9, for $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ or $NH_4Th_2(PO_4)_3$) with the ammonium ions (and water molecules) located in the tunnels.

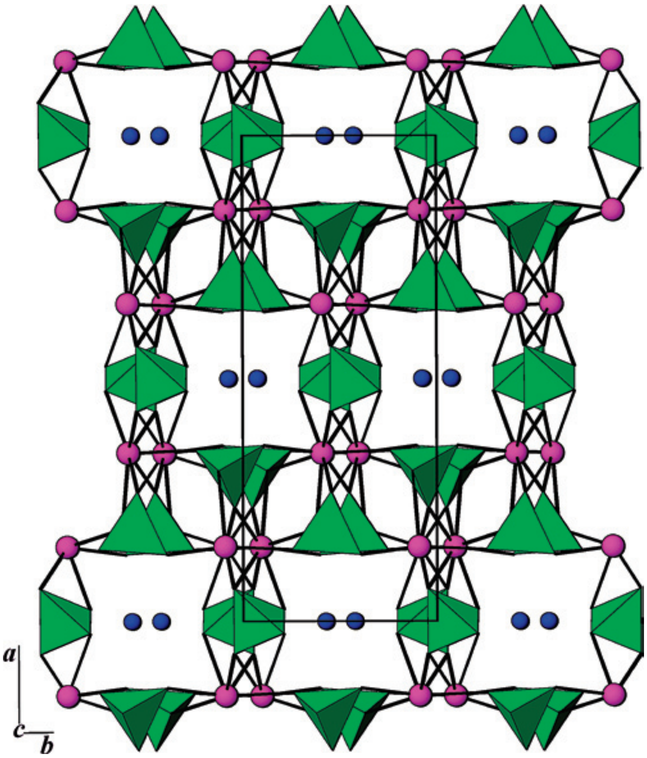

Figure 5. Representation of the structure of $NH_4Th_2(PO_4)_3$ along the *c* axis (for symbols, see Figure 4).

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Supporting Information Available: Fractional atomic coordinates for the new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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