

Chemistry of tetravalent actinide phosphates—Part I

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Abstract

The chemistry and crystal structure of phosphates of tetravalent cations, including that of actinides was reviewed several times up to 1985. Later, new compounds were synthesized and characterized. In more recent studies, it was found that some of previously reported phases, especially those of thorium, uranium and neptunium, were wrongly identified. In the light of these new facts an update review and classification of the tetravalent actinide phosphates is proposed in the two parts of this paper. Their crystal structure and some chemical properties are also compared to non-actinide cation phosphates.

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1. Introduction

The phosphates of two actinides, i.e., of thorium and uranium (IV) as well as of such tetravalent cations like Sn^{4+} , Ti^{4+} or Zr^{4+} were synthesized in the end of the 19th century. However, the real interest in this subject began since the 1950s and the literature in this field is very rich. Several authors published reviews concerning the chemistry of this kind of phosphates. A monograph on tetravalent element phosphates was published in 1972 by Tananaev [1], a chemistry of phosphates by Averbuch-Pouchot and Durif in 1994 [2], chemistry of condensed phosphates by Durif in 1995 [3] and the chemistry of actinide phosphates by Keller in 1972 [4] and Bamberger in 1985 [5].

Numerous phosphates of tetravalent cations, with various compositions were synthesized, but chemical formulae of the final products were often estimated taking into account the initial mole ratio of the reagents. Indeed, because of the very low solubility of the phosphates considered (even in strong and concentrated

acids), their compositions were not reachable using conventional analytical methods. Later, this problem was resolved by means of non-destructive methods of analysis like Electron Probe Micro Analysis (EPMA) or Particle Induced X-ray Emission (PIXE), etc. The characterization of new compounds or the reexamination of the known ones is supported now using various physico-chemical methods.

The classification of tetravalent cation phosphates is usually based on the $\text{P}:\text{M}^{4+}$ mole ratio. However, in this case, some difficulties are emerging because the same empirical composition can be often presented with different functional groups like: $\text{M}(\text{OH})\text{PO}_4$ and $(\text{MO})\text{HPO}_4$ or $\text{M}_2\text{O}(\text{PO}_4)_2$ and $(\text{MO})_2\text{P}_2\text{O}_7$. Other problems come out when the formulae of the compounds are given in the oxide form, e. g. $p\text{MO}_2 \cdot q\text{P}_2\text{O}_5$, $m\text{M}_2\text{O}$, $p\text{MO}_2 \cdot q\text{P}_2\text{O}_5$, $p\text{MO}_2 \cdot q\text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$. Sometimes, this kind of formulae may be presented taking into account functional groups (1). For example, the oxide form formula $2\text{TiO}_2 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ can be written as $\text{Ti}(\text{OH})\text{PO}_4 \cdot \text{H}_2\text{O}$ or $(\text{TiO})\text{HPO}_4 \cdot \text{H}_2\text{O}$. In such a case, it is necessary to prove the existence of the $\text{Ti}-\text{O}-\text{H}$ or $\text{Ti}=\text{O}$ and $\text{H}-\text{O}-\text{P}$ bonds in the compound. These problems can be solved by structural studies completed by physico-chemical investigations.

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Tetravalent cation phosphates like other crystallized inorganic solids are characterized first by means of XRD techniques. Complementary investigations such as UV-visible spectroscopy, vibration spectroscopy, XPS spectroscopy, NMR (^{31}P for phosphates and/or ^1H for hydrated and hydrogenphosphates), etc., are usually applied. These methods are very helpful because they allow to ascertain as well the oxidation state of the cation like U^{4+} , Np^{4+} , Pu^{4+} as the nature of different forms of phosphates in the solids: HPO_4^{2-} , PO_4^{3-} or condensed species $\text{P}_2\text{O}_7^{4-}$, $(\text{PO}_3)_n^n$. The most often used is the infrared (IR) (particularly in the 4000–400 cm^{-1} region) and/or Raman spectroscopy.

In the last 10 years, new phosphate compounds were obtained and characterized and the composition of some others, previously published, was revised. Thus, it was interesting to present these results in an up to date review. In the two parts of this paper, we review the chemistry of tetravalent actinide phosphates (Th, Pa, U, Np, Pu) in solid state. Their properties are compared to the phosphates of non-actinide tetravalent elements, mainly to Si, Sn, Pb, Ti, Zr, Hf and Ce. A systematic, based on the general framework formula $[(M^t)_m(A^q)_p]^k$ (where $k=hm+pq$), is also proposed. Three main families of derivative compounds result from this general formula:

- uncharged compounds for $k = 0$;
- cationic framework if $k > 0$, where the charge must be compensated by an anion $[(A^z)_y]^{y^z}$ (or both, anion and cation);
- anionic framework if $k < 0$, where the charge must be compensated by a cation $[(M^m)_x]^{m^x}$.

Applied to tetravalent cations M^{4+} and various phosphate anions $A^q = \text{H}_2\text{PO}_4^-$, HPO_4^{2-} , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, PO_3^- , the framework formula takes the $[(M_m(A^q)_p)]^k$ form with $k = 4m + pq$ and the following (combined) parameters:

$$q = -1 \text{ to } -4, \quad m = 1 \text{ to } 4, \quad p = 1 \text{ to } 6$$

for the M^{4+} cation

and for charge compensation ions:

$$n = 1, 2, \quad x = 1 \text{ to } 14, \quad y = 1, 2, \quad z \neq -3.$$

The three families of tetravalent cation phosphates are presented in Table 1. For $k < 0$, monovalent ($n = 1$) or divalent ($n = 2$) cations M are taken into account as compensation charge. When $k > 0$, the anion A ($z = -1, -2, -4$) may be either a simple (halogenide X^- or oxide O^{2-}) or a complex one (e.g. hydroxide, perchlorate, sulfate, silicate, etc.). Mixed actinide (IV) phosphates with $n = 4$ or $z = -3$ were not reported in the literature up to now. No publication about phosphates

Table 1
Families of tetravalent cation phosphates

Formula parameters			Framework	Phosphate formula	Compensation ions
$m = 1$	$q = -1$	$p = 4$	$k = 0$	$[(M)_m(A^q)_p]^k$	
	$q = -2$	$p = 2$		$\text{M}(\text{H}_2\text{PO}_4)_4$	
	$q = -4$	$p = 1$		$\text{M}(\text{PO}_3)_4$	
	$q = -3$	$p = 4$		$\text{M}(\text{HPO}_4)_2$	
$m = 3$	$q = -3$	$p = 4$		MP_2O_7	
$m = 1$	$q = -3$	$p = 4$		“ $\text{M}_3(\text{PO}_4)_4$ ”	
	$q = -1$	$p = 2$	$k > 0$	$[(M)_m(A^q)_p]^k$	
	$q = -2$	$p = 1$		$\text{M}(\text{H}_2\text{PO}_4)_2A_2$	$A = \text{ClO}_4$
	$q = -2$	$p = 1$		$\text{M}(\text{HPO}_4)A$	$A = \text{SO}_4$
	$q = -2$	$p = 2$		$\text{M}(\text{HPO}_4)_2A_2$	$A = \text{H}_2\text{PO}_4$
$m = p$	$q = -3$				
$m = 1$				MAPO_4	$A = X, A = \text{OH}$
$m = 2$				$\text{M}_2A(\text{PO}_4)_2$	$A = \text{O}, \text{HPO}_4$
					$A = \text{SO}_4$
$m = 4$				$\text{M}_4(\text{PO}_4)_4A$	$A = \text{P}_2\text{O}_7$
					$A = \text{SiO}_4$
$m = 1$	$q = -3$	$p = 2$	$k < 0$	$[(M)_m(A^q)_p]^k$	
		$p = 3$		$\text{M}_2\text{M}(\text{PO}_4)_2$	$M = \text{M(I)}$
		$p = 4$		$\text{MM}(\text{PO}_4)_2$	$M = \text{M(II)}$
		$p = 6$		$\text{M}_3\text{M}(\text{PO}_4)_3$	$M = \text{M(I)}$
				$\text{M}_8\text{M}(\text{PO}_4)_4$	$M = \text{M(I)}$
				$\text{M}_{14}\text{M}(\text{PO}_4)_6$	$M = \text{M(I)}$
				$\text{M}_7\text{M}(\text{PO}_4)_6$	$M = \text{M(II)}$
$m = 2$	$q = -3$	$p = 3$		$\text{MM}_2(\text{PO}_4)_3$	$M = \text{M(I)}$
					$M = 0.5 \text{ M(II)}$

With $k = 4m + pq$.

of tetravalent transplutonium elements was found. Only $M(\text{IV})$ phosphates of the uncharged framework are described in the first part of this work.

2. Phosphates of uncharged framework: $k=0$, $[\text{M}_m(\text{A}^q)_p]^k$

To this family belong compounds with parameter values equal to: $m=1$, $p=1, 2, 4$ and $q=-1, -2, -4$. Four groups are mentioned in the literature (Table 1): dihydrogenphosphates, hydrogenphosphates, two types of condensed phosphates and the controversial phosphates $\text{M}_3(\text{PO}_4)_4$ ($q=-3$, $p=4$, $m=3$).

2.1. Dihydrogenphosphates $\text{M}(\text{H}_2\text{PO}_4)_4$ ($q=-1$, $p=4$, $m=1$)

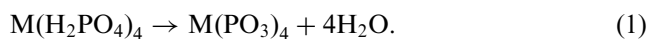
This kind of compounds was rarely studied. A plutonium compound of formula $\text{H}_4[\text{Pu}(\text{HPO}_4)_4] \cdot n\text{H}_2\text{O}$ that may be also presented as a dihydrogenphosphate $\text{Pu}(\text{H}_2\text{PO}_4)_4 \cdot n\text{H}_2\text{O}$ was described by Denotkina and Shevchenko [6]. It was precipitated from a mixture of plutonium (IV) solution with 1.2–1.6 M phosphoric acid in 2 M nitric acid. The product is soluble in concentrated nitric and hydrochloric acids but the ions are hydrolyzed in water. No reference was found for other actinide (IV) dihydrogenphosphates.

Besides the plutonium dihydrogenphosphate, silicon and lead (IV) ones are reported, although presented in different forms: $\text{H}_8[\text{Si}(\text{PO}_4)_4]$, $\text{H}_2[\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{HPO}_4)_2]$, $\text{Pb}(\text{H}_2\text{PO}_4)_4$. The first one, which formula can be also written $\text{Si}(\text{H}_2\text{PO}_4)_4$ was prepared from silica gel and phosphoric acid [7] while the two others (of the same empiric formula) were obtained through electrochemical method using lead electrodes in concentrated H_3PO_4 [8]. Heating of the lead tetra-acetate $\text{Pb}(\text{CH}_3\text{COO})_4$ with phosphoric acid is another way of synthesis of $\text{H}_2[\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{HPO}_4)_2]$ [8]. The complex $\text{Pb}(\text{H}_2\text{PO}_4)_4 \cdot 2\text{H}_3\text{PO}_4$ was obtained in similar conditions [8].

Both, $\text{H}_8[\text{Si}(\text{PO}_4)_4]$ and $\text{Pb}(\text{H}_2\text{PO}_4)_4$, are unstable in water: the first one is hydrolyzed to phosphoric H_3PO_4 and silicic $\text{H}_4\text{SiO}_4 \cdot n\text{H}_2\text{O}$ acids, while lead (IV) is reduced into lead (II) in the second one. No information was mentioned about the crystallized or amorphous state of all these compounds and no particular application was reported.

2.2. Polytrioxophosphates $\text{M}(\text{PO}_3)_4$ ($q=-1$, $p=4$, $m=1$)

This group of compounds (formerly called metaphosphates) should be considered as derivatives of dihydrogenphosphates leading through condensation to some polytrioxophosphate as follows:



However, no reference was found in the literature on this method.

Thorium and uranium (IV) polytrioxophosphates were obtained using various methods of synthesis: from an anhydrous thorium salt (chloride, bromide, sulfate) and polyphosphoric acid, by heating the gels obtained by mixing thorium or uranium salts solutions with phosphoric acid, etc. Both, $\text{Th}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$ are polymorphous. Three crystal forms are mentioned: orthorhombic [9–13], tetragonal [12] and triclinic [12] for thorium compound and orthorhombic [9,12–15], monoclinic [14] and triclinic [12] for uranium. Their unit cell parameters are given in Table 2.

According to Burdese and Borlera, $\beta\text{-Th}(\text{PO}_3)_4$ (probably monoclinic form) is stable up to 750 °C then transformed into the orthorhombic $\alpha\text{-Th}(\text{PO}_3)_4$ at higher temperatures [10]. The transition between both phases is irreversible. The uranium $\beta\text{-U}(\text{PO}_3)_4$ and $\alpha\text{-U}(\text{PO}_3)_4$ polytrioxophosphates (temperature of transition 810 °C) are analogous with the thorium ones. The orthorhombic $\text{U}(\text{PO}_3)_4$ was prepared by heating UO_2 with polyphosphoric acid [9]. These authors also reported the formation of a series of α -thorium–uranium polytrioxophosphate solid solutions [10].

Baskin [14] indexed the two forms of uranium (IV) polytrioxophosphates from single crystal. The uranium environment (c. n. 8) in the orthorhombic modification determined by Linde et al. [15] is shown in Fig. 1.

Protactinium (IV) polytrioxophosphate was prepared under argon atmosphere from a protactinium difluoride sulfate PaF_2SO_4 solution in 14 M phosphoric acid [16]. The solution was gradually heated up to 900 °C in order to eliminate the hydrogen fluoride, sulfur trioxide SO_3 and the excess of phosphoric anhydride. The crystallized residue was formulated as $\text{Pa}(\text{PO}_3)_4$ and was considered to be isostructural with the orthorhombic $\text{Th}(\text{PO}_3)_4$ and $\text{U}(\text{PO}_3)_4$.

Three forms of neptunium (IV) polytrioxophosphates are mentioned in the literature [17]: tetragonal $\alpha\text{-Np}(\text{PO}_3)_4$ (detected only in mixture with other forms), triclinic $\beta\text{-Np}(\text{PO}_3)_4$ and orthorhombic $\gamma\text{-Np}(\text{PO}_3)_4$. These compounds were obtained by dry chemistry method from neptunium dioxide NpO_2 and diammonium hydrogenphosphate $(\text{NH}_4)_2\text{HPO}_4$ after heating at 800, 900 and 950 °C, respectively.

Crystals of plutonium (IV) polytrioxophosphate, $\text{Pu}(\text{PO}_3)_4$, were grown by digestion of PuO_2 in polyphosphoric acid [13]. Only the orthorhombic form was identified. Cerium (IV), usually considered as a good surrogate of plutonium, forms also an orthorhombic polytrioxophosphate $\text{Ce}(\text{PO}_3)_4$ [12].

Two forms of zirconium polytrioxophosphate $\text{Zr}(\text{PO}_3)_4$, monoclinic [18] and orthorhombic [19], were reported (Table 2). Their crystal structure is built on ZrO_8 polyhedra where the oxygen atoms belong to the polyphosphate units of eight tetrahedra.

Table 2
Crystallographic data of polytrioxophosphates of tetravalent cations $M(\text{PO}_3)_4^a$

Compound	System	S.G.	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Ref.
Th(PO_3) ₄	Tetragonal	$I4/mmm$	11.44		14.98				[12]
	Triclinic	n.d.	15.51	8.251	8.796	117.80	112.32	89.14	[12]
Th(PO_3) ₄	Orthorhombic	$Pnab$	14.35	15.11	9.05				[10]
		$Pbcn$	6.947	15.12	9.069				[12]
Pa(PO_3) ₄	Orthorhombic	n.d.	6.969	8.959	15.009				[16]
U(PO_3) ₄	Orthorhombic	$Pbcn$	6.913	14.97	8.986				[12]
		$Pbcn$	6.907	14.947	8.986				[15]
		$Pnab$	8.95	14.94	6.89				[13]
		$Pbca$	13.80	14.92	9.00				[14]
			14.33	14.96	9.05				[10]
U(PO_3) ₄	Monoclinic	n.d.	23.42	13.02	23.00		n.d.		[14]
	Triclinic	n.d.	15.43	8.147	8.735	117.64	112.59	89.00	[12]
Np(PO_3) ₄	Tetragonal	$I4/mmm$	11.21		14.80				[17]
Np(PO_3) ₄	Triclinic	n.d.	15.25	8.092	8.699	117.72	112.55	88.80	[17]
Np(PO_3) ₄	Orthorhombic	$Cmca$	8.989	14.969	6.947				[17]
Pu(PO_3) ₄	Orthorhombic	$Pbcn$	6.860	14.835	8.903				b
		$Pnab$	8.93	14.89	6.87				[13]
Ce(PO_3) ₄	Orthorhombic	$Pbcn$	6.889	14.88	8.939				[12]
Zr(PO_3) ₄	Orthorhombic	$Pca2_1$	20.504	9.758	8.49				[19]
	Monoclinic	Cc	13.495	28.799	8.658		90.04		[18]

^aEight-fold coordination for orthorhombic and monoclinic varieties.

^bJCPDS 43-1105.

n.d.: Not determined.

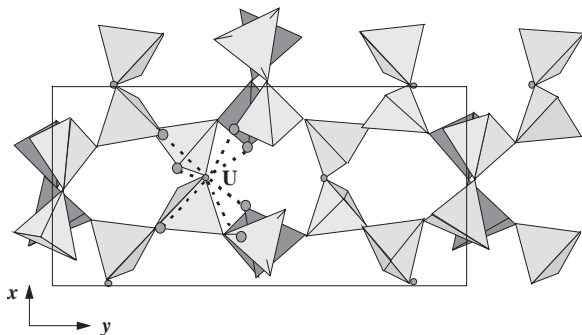


Fig. 1. Projection of the orthorhombic structure of $\text{U}(\text{PO}_3)_4$ along the $[001]$ direction [15].

The relationship between the unit cell volume and the Shannon's ionic radii [20] of M^{4+} cation for the orthorhombic forms is plotted in Fig. 2. This trend is linear, except for neptunium for which a and c unit cell parameters are surprisingly more extended compared to the uranium ones.

Generally, polytrioxophosphates are decomposed at high temperatures (protactinium and uranium under inert conditions) into diphosphates MP_2O_7 and P_4O_{10} .

2.3. Hydrogenphosphates $M(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($q=-2$, $p=2$, $m=1$)

These kinds of solids, where the number of water molecules n varies from 0 to 6, were largely investigated

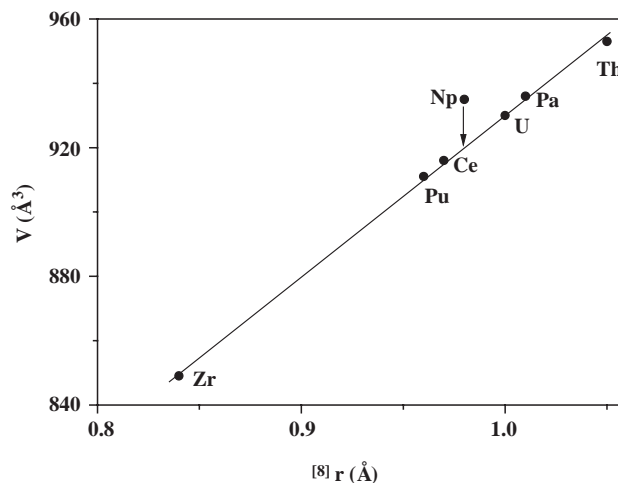


Fig. 2. Variation of the unit cell volume vs. M^{4+} ionic radius for orthorhombic polytrioxophosphates $M(\text{PO}_3)_4$.

because of ion-exchange properties characteristic for several of them. Among actinide hydrogenphosphates, the amorphous and fibrous $\text{Th}(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ (prepared by soft chemistry) was the most investigated ion-exchange material [21,22].

Uranium hydrogenphosphates $\text{U}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 1-6$) were precipitated from aqueous solutions of U^{4+} and phosphoric acid either as amorphous or crystallized solids [23,24]. $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ was also obtained in concentrated phosphoric acid [23]. The

XRD data of the crystallized uranium hydrogenphosphates were published by Dunn [25].

A plutonium compound, $\text{Pu}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$, was precipitated as a gelatinous solid in nitric acid solution [26]. Publications about protactinium and neptunium hydrogenphosphates were not found in literature.

The hydrogenphosphates of non-actinide element (Si–Pb, Ti–Hf and Ce) were more studied than the actinide ones. They were synthesized from a dioxide MO_2 or a water-soluble salt of the corresponding element using soft chemistry methods. Anhydrous and hydrated silicon or germanium compounds $\text{Si}(\text{HPO}_4)_2$ ([27,28] JCPDS File No. 21-1067), $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ [28], $\text{Ge}(\text{HPO}_4)_2$ ([28,29], JCPDS File No. 37-0671) $\text{Ge}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ([28,29], JCPDS File No. 37-0278) were reported. The symmetry group and the unit cell parameters were defined only for the hydrated compounds.

The most studied were the monoclinic layered $\alpha\text{-M}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ where $\text{M} = \text{Sn}, \text{Pb}, \text{Ti}, \text{Zr}, \text{Hf}, \text{Ce}$ (Table 3). Three forms of zirconium hydrogenphosphate were reported. $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\beta\text{-Zr}(\text{HPO}_4)_2$ (JCPDS Files No. 34-0127 and 32-1495, respectively) crystallize in the monoclinic system while there is no information for the γ modification [30]. Several authors studied the α form ($\alpha\text{-ZHP}$) but some discrepancies remain in the unit cell parameter values. Its crystal structure was determined by Clearfield et al. [31,32] and then by Dushin and Krylov [33]. It is made up of ZrO_6 layers of slightly distorted octahedra and alternating HPO_4 tetrahedra (Fig. 3). The water molecules occupy

the interlayer space. Bruque et al. [34,35] determined the unit cell parameters of tin, titanium and lead hydrogenphosphates and found these compounds isostructural with $\alpha\text{-ZHP}$. Germanium (JCPDS File No. 37-0278) and hafnium hydrogenphosphates [36] were of the same type. The crystal cell parameters and the structure of cerium (IV) hydrogenphosphate $\text{Ce}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ were not yet determined [37]. Several of the hydrogenphosphates described above (tin, titanium, zirconium and cerium) behave as cation exchangers [31,32,37–40].

The unit cell volume of $\alpha\text{-M}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is plotted vs. the M^{4+} ionic radii in Fig. 4. Note two linear trends in this figure: different for $d^{(n-1)} ns^2$ elements (Ti, Zr, Hf) and for the $ns^2 np^2$ ones (Ge, Sn, Pb). The ratio of the

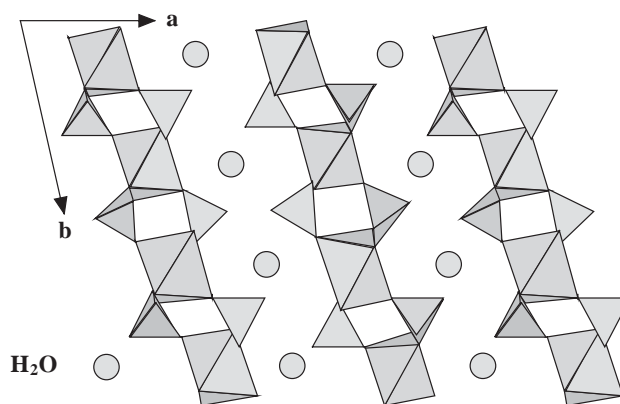


Fig. 3. Projection of the structure of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ [32] along the $[001]$ direction.

Table 3
Crystallographic data of hydrogenphosphates of non-actinide tetravalent cations^a

Compound	System	S.G.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Ref.
$\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	Monoclinic	$P2_1/n$	8.64	5.009	15.510	101.32	[35]
$\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	Monoclinic	$P2_1/n$	15.463	5.294	9.067	101.70	^b
		$P2_1/c$	9.070	5.298	16.22	111.5	[32,33]
$\text{Zr}(\text{HPO}_4)_2$	Monoclinic	n.d.	9.26	5.34	15.77	113.5	^c
$\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	Monoclinic	n.d.	5.384	6.637	12.395	98.68	^d
$\text{Hf}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	Monoclinic	$P2_1/n$	9.014	5.256	15.477	101.63	[36]
		$P2_1/c$	8.80	5.28	16.3	111.0	^e
$\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	n.d.						[28]
$\text{Ge}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	Monoclinic	$P2_1/n$	8.306	4.788	15.657	99.92	^f
$\text{Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	Monoclinic	$P2_1/n$	8.612	4.964	15.861	100.00	[35]
		$P2_1/c$	8.61	5.02	16.75	110.2	[34]
$\text{Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	Orthorhombic	n.d.	8.575	4.985	4.77		[33], ^g
$\text{Sn}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	Monoclinic	$P2_1/n$	8.640	4.997	16.007	100.35	[40]
$\text{Pb}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	Monoclinic	$P2_1/n$	8.624	4.987	16.125	100.61	[35]

^aSix-fold coordination number for monoclinic variety.

^bJCPDS 34-0127.

^cJCPDS 32-1495.

^dJCPDS 45-0068.

^eJCPDS 37-0272.

^fJCPDS 37-0278.

^gJCPDS 31-1397.

n.d.: Not determined.

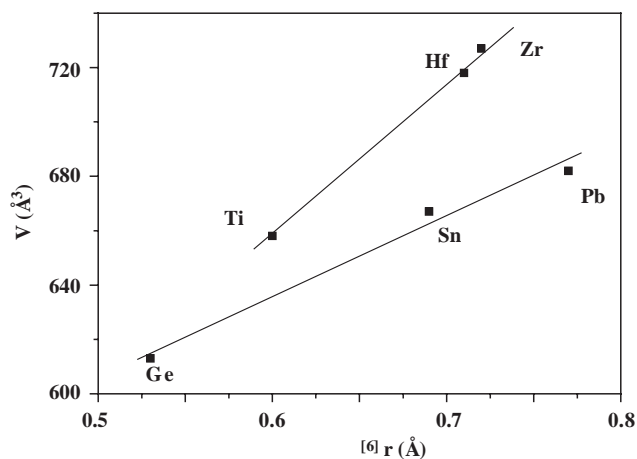
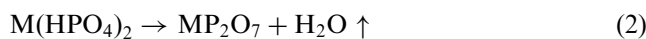


Fig. 4. Relationship between the unit cell volume and the ionic radii of M^{4+} for monoclinic hydrogenphosphates $M(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.

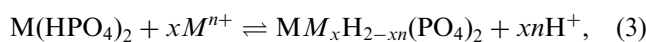
slopes (calculated from linear regression) is around 2.0. This observation is commented in the next section. Other crystallized hydrogenphosphates: $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (JCPDS File 45-0068), $\text{Sn}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ [41] and $\text{Ce}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (JCPDS File No. 49-0379) as well as the amorphous $\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ [38] were also reported.

All hydrated hydrogenphosphates are dehydrated at 200–250 °C then, at higher temperatures, HPO_4 groups are condensed into P_2O_7 entities. The temperature of condensation is generally spread over large limits depending on the cation considered. Thus, two main properties of hydrogenphosphates must be pointed:

Condensation:



and ion exchange:



$x = 1, 2$; $n = 1, 2$ (monovalent or divalent cation);
 $M = \text{Th}, \text{U}, \text{Ce}, \text{Zr}, \text{Ti}, \text{Sn}$.

2.4. Diphosphates MP_2O_7 ($q=-4, p=1, m=1$)

This group of compounds (traditionally called pyrophosphates) is one of the most investigated, even for elements such as rhenium (IV), molybdenum (IV) or platinum (IV), for which phosphates are not usually characteristic compounds. This category of solids was prepared by several ways of synthesis such as:

- Reactions, in aqueous solution, between the tetravalent cation and phosphating reagent such as sodium diphosphate, ammonium phosphate or concentrated phosphoric acid (the obtained precipitates are dried then calcined at high temperatures).
- Digestion of dioxide MO_2 (hydrated or dried) in concentrated phosphoric acid at about 250 °C.

- Dry chemistry methods by heating, at high temperature, a ground mixture of dioxide MO_2 and phosphate reagent like $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, BPO_4 or SiP_2O_7 .
- Thermal decomposition of polytrioxophosphates.
- Condensation of hydrogenphosphates.

The diphosphates obtained at high temperature are well-crystallized compounds. Their unit cell parameters are presented in Table 4. Thorium, uranium, silicon and germanium diphosphates are polymorphous. Except the monoclinic PtP_2O_7 [3], the cubic form named $\alpha\text{-MP}_2\text{O}_7$ is characteristic for all the elements. The crystal structure of this form was first determined for ZrP_2O_7 by Levi and Peyronel [42]. Six oxygen atoms of the P_2O_7 groups coordinate the zirconium ion. Other cubic diphosphates of tetravalent cations are isostructural with ZrP_2O_7 .

Two crystalline varieties of thorium and uranium diphosphates were obtained and characterized by several workers: the cubic ThP_2O_7 [10,43–45] and UP_2O_7 [10,44,46–49] and the orthorhombic ThP_2O_7 [10,44] and UP_2O_7 [10,50]. Burdese and Borlera also studied solid solutions of each couple of diphosphates: cubic $\text{ThP}_2\text{O}_7\text{--UP}_2\text{O}_7$ and orthorhombic $\text{ThP}_2\text{O}_7\text{--UP}_2\text{O}_7$ [51]. In the first system, 80% (in mole) of thorium was replaced by uranium (IV) while only 20% of uranium was introduced in the crystal structure of the second one. Mixed crystal forms were formed for higher values.

The structure of the cubic UP_2O_7 , determined by Cabeza et al. [49], belongs to the ZrP_2O_7 type where the UO_6 octahedra are linked through different diphosphate groups (Fig. 5).

The structure of the orthorhombic UP_2O_7 was recently determined from single crystal by Podor et al. [52]. This structure is built on UO_8 polyhedral chains with PO_4 tetrahedron and condensed linear P_3O_{10} groups. Thus, its right formula must be written as $\text{U}_2(\text{PO}_4)\text{P}_3\text{O}_{10}$ and should belong with such formulation to the $[\text{M}_m(\text{PO}_4)_p]^{(4m+pq)}$ group ($m = 2, p = 1, q = -3$, not mentioned in Table 1). According to its IR spectrum it seems to be hygroscopic (the band of H_2O bending mode appears at 1650 cm^{-1}). After heating at 870 °C, the compound is transformed into the more stable cubic UP_2O_7 . The unit cell parameters of the uranium phosphate-triphosphate are in good agreement with that determined by Douglas and Staritzky [50] and by Burdese and Borlera [51] for $\beta\text{-UP}_2\text{O}_7$. The orthorhombic ThP_2O_7 has the same structure than $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ [53].

The cubic protactinium diphosphate PaP_2O_7 was obtained by thermal decomposition of $\text{Pa}(\text{PO}_3)_4$ [16] while NpP_2O_7 was synthesized at high temperature from a mixture of NpO_2 and $(\text{NH}_4)_2\text{HPO}_4$ [17,54] or BPO_4 [44]. The plutonium PuP_2O_7 was first prepared by

Table 4
Crystallographic data of diphosphates of tetravalent cations^a

Compound	System	S.G.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Ref.
ThP ₂ O ₇	Cubic	<i>Pa</i> 3	8.721				[10]
	Orthorhombic	<i>Pna</i> 2 ₁	11.62	12.75	7.12		[10]
Th ₂ (PO ₄)P ₃ O ₁₀	Orthorhombic	<i>Pn</i> 2 ₁ <i>a</i>	11.678	7.171	12.925		[53] ^b
PaP ₂ O ₇	Cubic	<i>Pa</i> 3	8.65				[16]
UP ₂ O ₇	Cubic	<i>Pa</i> 3	8.627				[47]
			8.631				[49]
U ₂ (PO ₄)P ₃ O ₁₀	Orthorhombic	<i>Pn</i> 2 ₁ <i>a</i>	11.526	7.048	12.807		[52] ^b
			11.526	12.81	7.045		[50]
			11.521	12.767	7.044		[51]
NpP ₂ O ₇	Cubic	<i>Pa</i> 3	8.582				[17]
			8.565				[54]
			8.586				[75]
PuP ₂ O ₇	Cubic	<i>Pa</i> 3	8.560				[55]
			8.562				[5,44]
CeP ₂ O ₇	Cubic	<i>Pa</i> 3	8.338				[45]
			8.58				[57]
			8.607				[61]
			7.83				[42,57]
TiP ₂ O ₇	Cubic	<i>Pa</i> 3	7.83				[42,57]
ZrP ₂ O ₇	Cubic	<i>Pa</i> 3	8.252				[42]
			8.245				[9]
			8.247				[59]
HfP ₂ O ₇	Cubic	<i>Pa</i> 3	8.18				[42]
			8.186				^c
MoP ₂ O ₇	Cubic	<i>Pa</i> 3	7.944				^d
ReP ₂ O ₇	Cubic	<i>Pa</i> 3	7.94				[63]
PtP ₂ O ₇	Monoclinic	<i>P</i> 2 ₁ / <i>n</i>	7.095	7.883	9.302	111.37	[3]
SiP ₂ O ₇	Cubic	<i>Pa</i> 3	7.47				[42]
	Tetragonal	n.d.	22.4		14.19		[64]
	Hexagonal	<i>P</i> 6 ₃ / <i>m</i>	8.18		11.82		[64]
	Monoclinic	<i>P</i> 2 ₁ / <i>h</i>	4.73	12.02	7.62	90.1	[64]
GeP ₂ O ₇	Cubic	<i>Pa</i> 3	7.618				[57]
			7.607				[47]
	Monoclinic	<i>P</i> 2 ₁ / <i>c</i>	4.787	6.48	15.04	90.4	[3]
SnP ₂ O ₇	Cubic	<i>Pa</i> 3	7.975				[42,65]
PbP ₂ O ₇	Cubic	<i>Pa</i> 3	8.01				[42,45]

^aSix-fold Coordination for cubic variety and eight-fold coordination for the orthorhombic variety.

^bFormerly called β -MP₂O₇.

^cJCPDS 37-1494.

^dJCPDS 84-1794.

n.d.: Not determined.

heating a mixture of Pu(IV) solution with oxalic and phosphoric acids [55]. Later, this compound was also obtained by heating a mixture of PuO₂ and BPO₄ above 950 °C [56].

The cubic diphosphates of non-actinide tetravalent elements [27–29,42,45,47,57–64] are isotopic with ZrP₂O₇ and UP₂O₇. The unit cell parameters of all known MP₂O₇ compounds are listed in Table 4 and the variation of their unit cell volume vs. the cationic radius is depicted in Fig. 6. As for the hydrogenphosphates the slope of the straight line for the *d* and *f* elements is different from that of *sp* ones. The phenomenon should have some origin in the electronic configuration differences between *d* and *f* and *sp* elements and in shorter M(IV)–O distances for M = Si, Ge, Sn, Pb [65].

Völlenkle et al. [57] made a similar observation and plotted the *a*₀ parameter vs. the M⁴⁺ ionic radius, but in this case the function was not linear.

Several authors [65,66] extensively studied the infrared and Raman spectra of the cubic MP₂O₇ compounds. The problem of the linearity (or not) of the P–O–P group was especially discussed. The local symmetry in the PO₃ pyramid of the P₂O₇ group was not clear but is now considered as C_{2v} (or pseudo C_{2v}). The weak band (sometimes present as a doublet) observed in the 750–700 cm⁻¹ domain is assigned to the ν_s (P–O–P) vibration and its non-linearity is now accepted for all diphosphates of tetravalent cations. The ν_{as} (P–O–P) vibration, usually pointed at 950 cm⁻¹, often overlap with ν_s (P–O).

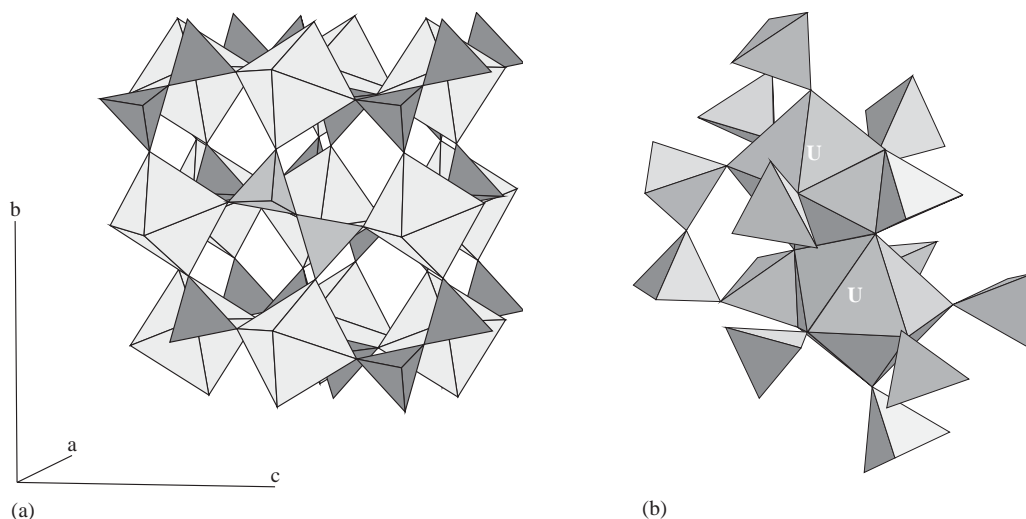


Fig. 5. View of the framework of (a) UP_2O_7 [49] and (b) $\text{U}_2(\text{PO}_4)\text{P}_3\text{O}_{10}$ [52].

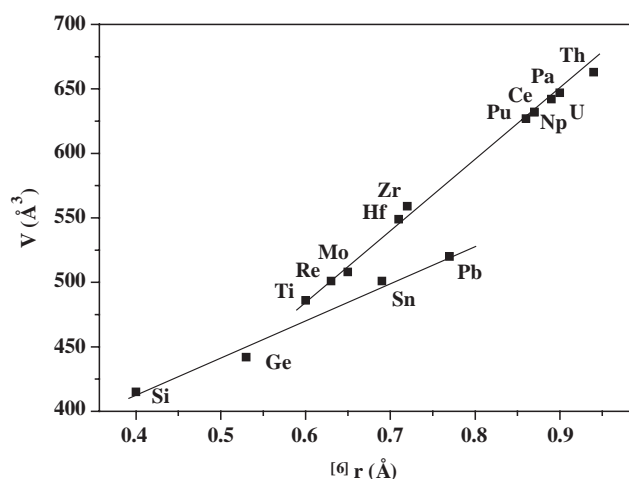


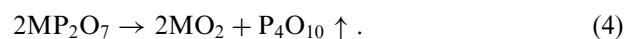
Fig. 6. Variation of the unit cell volume vs. the ionic radius for cubic diphosphates MP_2O_7 .

Hubin and Tarte [66] studied the role of the M^{4+} cation ($\text{M} = \text{Si}, \text{Sn}, \text{Pb}, \text{Ti}, \text{Zr}, \text{Hf}, \text{U}$) on the frequencies in the cubic diphosphates. These authors plotted the frequency intensities (the strong and medium bands) of P–O and P–O–P bond in terms of M^{4+} ionic radius. The increase of the ionic radius leads to the shift of the stretching frequencies to the lower values for $\text{M} = \text{Si}, \text{Sn}, \text{Pb}$ (*sp* elements) and to the higher values for $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ (*d* elements). On the other hand, for $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{U}$ the deformation frequencies are shifted to the lower values. Chung-Hsi Huang et al. [65] studied the same problem but could not draw clear conclusions, probably because of some differences in the results compared to that of Hubin and Tarte. Furthermore, it is even less clear taking into account the IR spectra of CeP_2O_7 [63], ThP_2O_7 [67], ReP_2O_7 [67] and UP_2O_7 [68].

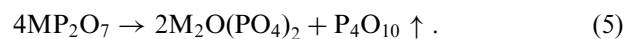
Syntheses and XRD data of a series of “actinyl(IV)” diphosphates $(\text{ThO})_2\text{P}_2\text{O}_7$ [10], $(\text{UO})_2\text{P}_2\text{O}_7$ [10,25,44,46], $(\text{NpO})_2\text{P}_2\text{O}_7$ [44], $(\text{PuO})_2\text{P}_2\text{O}_7$ [56] as well uranium species such as $(\text{U}_2\text{O}_3)_2\text{P}_2\text{O}_7$ [25,44,48,69–71] and $(\text{U}_3\text{O}_5)_2\text{P}_2\text{O}_7$ [69–71] were published in the past. However, the preparation of the thoryl diphosphate $(\text{ThO})_2\text{P}_2\text{O}_7$ was unsuccessful [44]. In the 1990s, the chemistry of uranium (IV), neptunium (IV) and plutonium (IV) phosphates was also reconsidered. From these investigations, it appeared that $(\text{U}_3\text{O}_5)_2\text{P}_2\text{O}_7$ was a polyphase system [72] while $(\text{U}_2\text{O}_3)_2\text{P}_2\text{O}_7$ corresponded to a mixed-valence uranium–uranyl phosphate $\text{U}(\text{UO}_2)(\text{PO}_4)_2$ [68,72,73]. Moreover, the compounds of $(\text{UO})_2\text{P}_2\text{O}_7$ and $(\text{NpO})_2\text{P}_2\text{O}_7$ formulae were identified in fact as diuranium oxide phosphate $\text{U}_2\text{O}(\text{PO}_4)_2$ [74] and dineptunium oxide phosphate $\text{Np}_2\text{O}(\text{PO}_4)_2$ [75].

The thermal decomposition of diphosphates occurs at higher temperatures than that of polytrioxophosphates (generally in the range of 1250–1350 °C). Rhenium diphosphate ReP_2O_7 , which begins to decompose at 750 °C under inert atmosphere, appears as an exception from this series. The resulting products of decomposition depend on the nature of the M element:

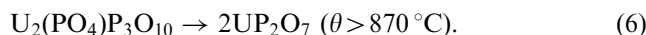
- Dioxides MO_2 and phosphorus (V) oxide from tin and rhenium diphosphates [76] according to the reaction:



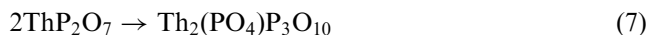
- Oxide phosphates from zirconium, hafnium [76], uranium (under inert atmosphere) and neptunium [72,74,75]:



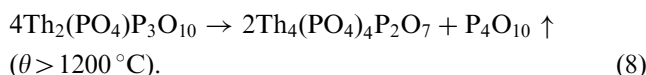
The metastable orthorhombic $U_2(PO_4)P_3O_{10}$ is first transformed into the cubic UP_2O_7 [52]:



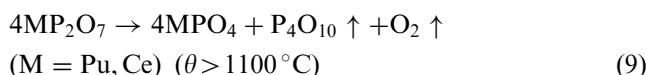
Contrary to the uranium compound, the cubic form of thorium diphosphate is transformed into the most stable orthorhombic $Th_2(PO_4)P_3O_{10}$



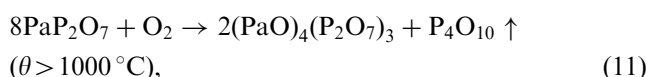
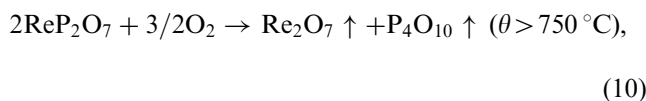
then this one into the thorium phosphate-diphosphate [77]:



The reactions of plutonium (IV) and cerium (IV) diphosphates in air are accompanied by a reduction process of the M element into MPO_4 (monazite structure) [56,78]:



while rhenium [76], protactinium [16] or uranium [68,72] are oxidized (in air atmosphere) according to the following reactions:



PaP_2O_7 was partly oxidized even under inert atmosphere into $(PaO)_4(P_2O_7)_3$, which decomposes at $1400^\circ C$ leading finally to Pa_2O_5 and P_4O_{10} [16]. In all cases, the ultimate decomposition products are a metal oxide and P_4O_{10} .

The precipitation of hydrated diphosphates $MP_2O_7 \cdot nH_2O$ (with variable number of water molecules) from solutions of thorium, uranium and cerium salts was also described in the literature [1]. For all these species, no information neither about their crystal state nor about their XRD data was reported. Their existence seems to be doubtful.

2.5. Phosphates " $M_3(PO_4)_4$ " ($q=-3$, $p=4$, $m=3$)

Some amorphous, hydrated thorium phosphates (obtained from solutions of thorium nitrate or chloride

and phosphoric acid or sodium phosphate) containing variable molecules of water $Th_3(PO_4)_4 \cdot nH_2O$ ($n = 5, 14, 17$) were reported in the past [79,80]. However, critical remarks appeared considering additional studies based for example on infrared (IR) spectroscopy and 1H NMR. For example, the phosphate $Th_3(PO_4)_4 \cdot 5H_2O$ was presented as $Th_3(OH)_2(HPO_4)_2(PO_4)_2 \cdot 3H_2O$ [1]. Nevertheless, the purity of such species, which can be a mixture of several compounds of the same global composition, was not demonstrated. The interpretation of the IR spectra of the amorphous $Th_3(PO_4)_4 \cdot nH_2O$ leads to some confusions: the P–O vibration frequencies were compared to that of crystallized anhydrous $LaPO_4$ (or $GdPO_4$) and an assumption was made that these products exhibit the same structure [80]. It seems that these precipitates are mixed phase systems containing various hydrogenphosphates.

$U_3(PO_4)_4 \cdot nH_2O$ similar to $Th_3(PO_4)_4 \cdot nH_2O$ was also described [1]. A compound of a presumably formula $Pu_3(PO_4)_4 \cdot nH_2O$ was obtained from plutonium (IV) and phosphoric acid solutions [26]. Both compounds could be also polyphase.

The chemistry of anhydrous phosphates of general formula " $M_3(PO_4)_4$ " is also controversial. " $Th_3(PO_4)_4$ " was obtained either by dehydration and further calcination of a gel formed in a mixture with mole ratio $H_3PO_4:Th^{4+} = 1.33$ in acid solutions [45,81], or of the hydrated $Th_3(PO_4)_4 \cdot nH_2O$ [79]. It was also prepared by dry way of synthesis from ThO_2 and $NH_4H_2PO_4$ [43,44]. Its XRD pattern was published by several authors [10,43,81] and the system was found to be monoclinic with the following unit cell parameters: $a = 10.55 \text{ \AA}$, $b = 10.66 \text{ \AA}$, $c = 8.80 \text{ \AA}$ and $\beta = 106.41^\circ$. However, Tanaev et al. [82] showed that when heated at $900^\circ C$, $Th_3(PO_4)_4 \cdot nH_2O$ was decomposed into ThO_2 and a second compound formulated as $ThO_2 \cdot 0.8P_2O_5$. Later, it was proved that for this initial composition of the reactants (P:Th=1.33) the mixture obtained at high temperature was composed of ThO_2 and of a new phase of global formula $Th_4P_6O_{23}$. From EPMA results and structure determination from single crystal and X-ray powder diffraction data, this compound was identified as the thorium phosphate-diphosphate (TPD) $Th_4(PO_4)_4P_2O_7$ [77].

The XRD pattern of " $U_3(PO_4)_4$ " was reported for the first time by Dunn [25]. It was determined by Burdese and Borlera [10] in the monoclinic system with the unit cell parameters: $a = 10.78 \text{ \AA}$, $b = 10.76 \text{ \AA}$, $c = 9.12 \text{ \AA}$ and $\beta = 104.7^\circ$ as analogous to " $Th_3(PO_4)_4$ ". Nevertheless, Bamberger et al. [44] were unable to synthesize neither " $U_3(PO_4)_4$ " nor " $Np_3(PO_4)_4$ " at $1000^\circ C$. The plutonium (IV) analogue " $Pu_3(PO_4)_4$ " was not also obtained [78]. Moreover, the systems schematically presented as $MO_2 \cdot P_2O_5$ ($M = Th, U, Np, Pu$), with mole ratio P:M = 1.33, ended to polyphase at high temperatures (Table 5).

Table 5
Actinide phosphate systems obtained for the initial mole ratio P:M = 1.33

Supposed formula	Heating conditions	Compounds obtained	Ref.
“Th ₃ (PO ₄) ₄ ”	1100–1250 °C, air	Th ₄ (PO ₄) ₄ P ₂ O ₇ + ThO ₂	[77]
“U ₃ (PO ₄) ₄ ”	1200 °C, air	UP ₂ O ₇ + U(UO ₂)(PO ₄) ₂	[68]
“U ₃ (PO ₄) ₄ ”	1250 °C, argon	UP ₂ O ₇ + U ₂ O(PO ₄) ₂	[68,72]
“Np ₃ (PO ₄) ₄ ”	1000 °C, air	NpP ₂ O ₇ + Np ₂ O(PO ₄) ₂ + NpO ₂	[75]
“Pu ₃ (PO ₄) ₄ ”	1000 °C, air	PuP ₂ O ₇ + PuPO ₄	[78]

Table 6
Phosphates of tetravalent cations of [(M)_m(A^q)_p]^k family with k = 0

Compound	Th	Pa	U	Np	Pu	Ce	Ti	Zr	Hf	Re	Mo	Si	Ge	Sn	Pb
M(H ₂ PO ₄) ₄ ^a	–	–	–	–	+	–	–	–	–	–	–	+	–	–	+
M(PO ₃) ₄	+	+	+	+	+	+	–	+	–	–	–	–	–	–	–
M(HPO ₄) ₂ ^a	+ ^b	–	+ ^c	–	+ ^b	+	+	+	+	–	–	+	+	+	+
MP ₂ O ₇ (cubic)	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

^ahydrated or anhydrous compounds.

^bNo XRD pattern found in literature.

^cOnly XRD pattern found in literature.

–, References not found.

The crystal system for “M₃(PO₄)₄” was defined as monoclinic for M = Zr, Sn and hexagonal for M = Si (JCPDS File No. 22-1380). No crystallographic data were reported for phosphates with M = Ge, Hf, Ce. It is also not clear whether “Zr₃(PO₄)₄” [61,82,83], “Hf₃(PO₄)₄” [62] and “Sn₃(PO₄)₄” [84] are real and pure compounds. Indeed, the XRD diagrams of the zirconium phosphate “Zr₃(PO₄)₄” reveals some XRD lines of the dizirconium oxide phosphate Zr₂O(PO₄)₂ [85]. The conclusion for “Hf₃(PO₄)₄” published by Mal’shikov and Bondar’ [62] is not very clear. A band located at 745 cm⁻¹, usually attributed to the P₂O₇ group (P–O–P bridge), appears in the IR spectrum presented. The existence of this band, first mentioned in the text then denied by the authors, is in contradiction to the proposed formula. In more recent experiments, these three systems were found to be polyphase: composed of ZrP₂O₇ + Zr₂O(PO₄)₂ and of MP₂O₇ + MO₂ for hafnium and tin [76].

3. Conclusions

Phosphates of tetravalent elements were intensively investigated in the last 50 years. In this paper, a review of tetravalent actinide phosphates referred in the literature is presented. Their crystal structures and chemical properties are compared to that of non-actinide elements.

A classification of tetravalent cation phosphates based on the framework [(M)_m(A^q)_p]^k with k = 4m + pq

is proposed (Table 1). In this framework, A represents an anion (simple or condensed) derived from phosphoric acid H₃PO₄. In the first part of the article, phosphates of uncharged framework (k = 0), e.g., dihydrogen-phosphates M(H₂PO₄)₄·nH₂O, hydrogen-phosphates M(HPO₄)₂·nH₂O, two types of condensed phosphates M(PO₃)₄ and MP₂O₇ are described. For all the elements studied, the controversial “M₃(PO₄)₄” compounds seem to correspond to polyphase systems. A summary of the phosphates reported for k = 0 is given in Table 6. Among these solids, the crystal structure of diphosphates was the most often investigated. Zirconium and titanium (IV) hydrogenphosphates were intensively studied as cation exchangers and proposed for the decontamination of high-level radioactive liquid waste among other applications [86–88].

Acknowledgments

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References

- [1] I.V. Tananaev (Ed.), The Chemistry of Tetravalent Elements Phosphates, Nauka, Moscow, 1972.
- [2] M.T. Averbuch-Pouchot, A. Durif (Eds.), Topics in Phosphate Chemistry, World Scientific, Singapore, 1994.

- [3] A. Durif, *Crystal Chemistry of Condensed Phosphates*, Plenum Press, New York, London, 1995.
- [4] C. Keller, *Transurane phosphate*, in: *Gmelins Handbuch der Anorganische Chemie*, Verlag Chemie, Weinheim, 1972, part C, pp. 269–276.
- [5] C.E. Bamberger, in: J. Freeman, C. Keller (Eds.), *Handbook on the Physics and Chemistry of the Actinides*, Elsevier, Amsterdam, 1985, pp. 289–303.
- [6] R.G. Denotkina, V.B. Shevtchenko, *J. Inorg. Chem.* 6 (1961) 1476 (Russ. Ed.).
- [7] R. Schwarz, *Z. Anorg. Allg. Chem.* 176 (1928) 236.
- [8] F. Huber, M.S.A. El-Meligy, *Z. Anorg. Allg. Chem.* 367 (1969) 154.
- [9] A. Burdese, M.L. Borlera, *Ric. Sci. Ital.* 30 (1960) 103.
- [10] A. Burdese, M.L. Borlera, *Ann. Chim. Roma* 53 (1963) 344.
- [11] E. Torraca, *J. Inorg. Nucl. Chem.* 31 (1969) 1189.
- [12] R. Masse, J.C. Grenier, *Bull. Soc. Fr. Minér. Crist.* 95 (1972) 136.
- [13] R.M. Douglas, *Acta Crystallogr.* 15 (1962) 505.
- [14] J. Baskin, *J. Inorg. Nucl. Chem.* 29 (1967) 383.
- [15] S.A. Linde, Y.E. Gorbunova, V.V. Il'ukhin, V.G. Kuznetsov, A.V. Lavrov, *J. Inorg. Chem.* 24 (1979) 1786 (Russ. Ed.).
- [16] M.F. Le Cloarec, A. Cazaussus, *J. Inorg. Nucl. Chem.* 40 (1978) 1680.
- [17] F. Nectoux, A. Tabuteau, *Radiochem. Radioanal. Lett.* 49 (1981) 43.
- [18] Y.E. Gorbunova, V.V. Il'ukhin, V.G. Kuznetsov, A. V. Lavrov, S.A. Linde, *Dokl. Akad. Nauk SSSR* 228 (1976) 1329.
- [19] Y.E. Gorbunova, V.V. Il'ukhin, V.G. Kuznetsov, A.V. Lavrov, S.A. Linde, *Dokl. Akad. Nauk SSSR* 234 (1977) 628.
- [20] R.D. Shannon, *Acta Crystallogr.* 5 (1975) 12.
- [21] G. Alberti, A. Conte, E. Torraca, *J. Inorg. Nucl. Chem.* 28 (1966) 225.
- [22] A.K. De, K. Chowdhury, *J. Chromatogr.* 101 (1974) 63.
- [23] J.M. Schreyer, *J. Am. Chem. Soc.* 77 (1955) 2972.
- [24] L.V. Kobets, T.A. Kolevich, D.S. Umreiko, *Russ. J. Inorg. Chem.* 22 (1977) 1025.
- [25] H.W. Dunn, X-ray diffraction data for some uranium compounds ORNL, Oak Ridge National Laboratory, Oak Ridge, TN 2092, 1956.
- [26] E.L. King, in: G.T. Seaborg, J.J. Katz, W.M. Manning (Eds.), *The Transuranium Elements*, McGraw-Hill, New York, 1949, pp. 638–645.
- [27] J. Gobeau, K.O. Christe, W. Teske, W. Wilborn, *Z. Anorg. Allg. Chem.* 325 (1963) 26.
- [28] B. Lelong, *Ann. Chim.* 9 (1964) 229.
- [29] K.A. Avduevskaya, I.V. Tananaev, *Russ. J. Inorg. Chem.* 8 (1963) 1020.
- [30] La Ginestra, A. Massucci, *Thermochim. Acta* 32 (1979) 241.
- [31] A. Clearfield, J.A. Stynes, *J. Inorg. Nucl. Chem.* 26 (1964) 117.
- [32] A. Clearfield, S.D. Smith, *Inorg. Chem.* 8 (1969) 431.
- [33] R. Dushin, R. Krylov, *Inorg. Mater.* 14 (1978) 216.
- [34] E. Rodriguez-Castellon, A. Rodriguez, S. Bruque, *Inorg. Chem.* 24 (1984) 1187.
- [35] S. Bruque, M.A.G. Aranda, E.R. Losilla, P. Olivera-Pastor, P. Maireles-Tores, *Inorg. Chem.* 34 (1995) 893.
- [36] I. Nakai, K. Imai, T. Kawashima, K. Ohsumi, F. Izumi, I. Tomita, *Anal. Sci.* 6 (1990) 689.
- [37] G. Alberti, U. Costantino, F. Di Gregorio, P. Galli, E. Torraca, *J. Inorg. Nucl. Chem.* 30 (1968) 295.
- [38] G. Alberti, M.G. Bernasconi, M. Casciola, U. Costantino, *J. Inorg. Nucl. Chem.* 42 (1980) 1637.
- [39] M.J. Fuller, *J. Inorg. Nucl. Chem.* 33 (1971) 559.
- [40] A.I. Bortun, L.N. Bortun, A.A. Stepin, N.P. Pekhamkina, *J. Radioanal. Nucl. Chem.* 174 (1993) 279.
- [41] A.B. Yaroslavtsev, Z.N. Prozorovskaya, V.F. Chuvaev, B.F. Parshutkin, G.G. Shifanova, *Russ. J. Inorg. Chem.* 34 (1989) 1188.
- [42] G.R. Levi, G. Peyronel, *Z. Kristallogr.* 92A (1935) 190.
- [43] K.R. Laud, F.H. Hummel, *J. Am. Ceram. Soc.* 54 (1971) 296.
- [44] C.E. Bamberger, R.G. Haire, G.M. Begun, H.E. Hellwege, *J. Less-Common Metals* 102 (1984) 179.
- [45] M.L. Borlera, A. Burdese, *Atti. Acad. Sci. Torino* 94 (1959–1960) 91.
- [46] H.P. Kirchner, K.M. Merz, W.R. Brown, *J. Am. Ceram. Soc.* 46 (1963) 137.
- [47] L.-O. Hagman, P. Kierkegaard, *Acta Chem. Scand.* 23 (1969) 327.
- [48] C.E. Bamberger, G.M. Begun, D.E. Heatherly, *J. Am. Ceram. Soc.* 66 (1983) C-208.
- [49] A. Cabeza, M.A.G. Aranda, D. Lozano, M. Martinez-Lara, S. Bruque, *J. Solid State Chem.* 121 (1996) 181.
- [50] R.M. Douglas, E. Staritzky, *Anal. Chem.* 28 (1956) 1211.
- [51] A. Burdese, M.L. Borlera, *Ann. Chim. Roma* 53 (1963) 333.
- [52] R. Podor, M. François, N. Dacheux, *J. Solid State Chem.* 172 (2003) 66.
- [53] M. François, R. Podor, Université H. Poincaré—Nancy I (France), private communication.
- [54] C. Keller, K.H. Walter, *J. Inorg. Nucl. Chem.* 27 (1965) 1253.
- [55] C.W. Bjorklund, *J. Amer. Chem. Soc.* 79 (1958) 6347.
- [56] C.E. Bamberger, R.G. Haire, H.E. Hellwege, G.M. Begun, *J. Less Common Metals* 97 (1984) 349.
- [57] H. Völlenkne, A. Wittman, H. Nowotny, *Monatsh. Chem.* 94 (1963) 956.
- [58] D.E. Harrison, H.A. McKinstry, F.A. Hummel, *J. Am. Ceram. Soc.* 37 (1954) 277.
- [59] M. Chaunac, *Bull. Soc. Chim. Fr.* 2 (1971) 424.
- [60] R. Pascard, M. Chaunac, E. Grison, *Bull. Soc. Chim. Fr.* 2 (1971) 429.
- [61] I.L. Botto, E.J. Baran, *Z. Anorg. Allg. Chem.* 430 (1977) 283.
- [62] A.E. Mal'shikov, I.A. Bondar', *Russ. J. Inorg. Chem.* 34 (1989) 1207.
- [63] E. Banks, R. Sacks, *Mater. Res. Bull.* 17 (1982) 1053.
- [64] F. Liebau, G. Bissert, *Bull. Soc. Chim. Fr. Numéro Spécial* (1968) 1742.
- [65] C.-H. Huang, O. Knop, D.A. Othen, F.W.D. Woodhams, R.A. Howie, *Canad. J. Chem.* 53 (1975) 79.
- [66] R. Hubin, P. Tarte, *Spectrochim. Acta* 23A (1967) 1815.
- [67] H. Catalette, K. Popa, Institut de Physique Nucléaire, Orsay (France), private communication.
- [68] N. Dacheux, V. Brandel, M. Genet, *New. J. Chem.* 19 (1995) 15.
- [69] J.M. Schaekers, W.G. Greybe, *J. Appl. Chem.* 6 (1973) 245.
- [70] J.M. Schaekers, *J. Therm. Anal.* 6 (1974) 145.
- [71] H. Barten, E.H.P. Cordfunke, *Thermochim. Acta* 40 (1980) 357.
- [72] V. Brandel, N. Dacheux, M. Genet, *J. Solid State Chem.* 121 (1996) 467.
- [73] P. Bénard, D. Louër, N. Dacheux, V. Brandel, M. Genet, *Chem. Mater.* 6 (1994) 1049.
- [74] P. Bénard, D. Louër, N. Dacheux, M. Genet, *Anal. Quimica* 92 (1996) 79.
- [75] N. Dacheux, A.C. Thomas, V. Brandel, M. Genet, *J. Nucl. Mater.* 257 (1998) 108.
- [76] S. Poisson, K. Popa, Institut de Physique Nucléaire, Orsay (France), private communication.
- [77] P. Bénard, V. Brandel, N. Dacheux, S. Jaulmes, S. Launay, C. Lindecker, D. Louër, M. Genet, M. Quarton, *Chem. Mater.* 8 (1996) 181.
- [78] N. Dacheux, R. Podor, V. Brandel, M. Genet, *J. Nucl. Mater.* 252 (1998) 179.
- [79] A.K. Molodkin, T.A. Balakeeva, A.N. Kutchumova, *Dokl. Akad. Nauk SSSR* 165 (1965) 573.

- [80] A.K. Molodkin, K.I. Petrov, T.A. Balakeeva, A.N. Kutsumova, *Russ. J. Inorg. Chem.* 13 (1968) 1654.
- [81] J. Shankar, P.G. Khubchandani, *Anal. Chem.* 29 (1957) 1375.
- [82] I.V. Tananaev, I.A. Rozanov, E.N. Beresnev, *Inorg. Mater.* 12 (1975) 882.
- [83] J. Alamo, R. Roy, *J. Am. Ceram. Soc.* 67 (1984) C-78.
- [84] M. Mathew, L.W. Schroeder, T.H. Jordan, *Acta. Crystallogr* 33 (1977) 1812.
- [85] W. Gebert, E. Tillans, *Acta Crystallogr B* 31 (1975) 1768.
- [86] A.I. Bortun, L.N. Bortun, A.A. Stepi, N.P. Pekhamkina, *J. Radioanal. Inorg. Nucl. Chem.* 174 (1993) 279.
- [87] M. Zamin, T. Shaheen, A Dyer, *J. Radioanal. Inorg. Nucl. Chem.* 182 (1994) 323.
- [88] A.I. Bortun, L.N. Bortun, S.A. Khainakov, J.I. García Alonso, J.R. Garcia, A. Clearfield, *Solvent Extraction Ion Exchange* 15 (1997) 895.