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Inorganic–organic hybrid materials: synthesis and crystal structure determination from powder diffraction data of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$

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Abstract

A new lead diphosphonate, $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$ was hydrothermally synthesized from tetraethyl α,α'-*p*-xylenediphosphonate and $Pb(NO_3)_2$. The structure was solved and refined using X-ray powder diffraction data. It crystallizes in the monoclinic space group $P2_1/c$, with $a = 467.84(2)$, $b = 2007.98(9)$, $c = 639.10(2)$ pm, $\beta = 101.020(3)^\circ$, $V = 589.31(4)\ 10^6$ pm, $Z = 2$, $wR_p = 0.034$, $R_p = 0.027$, $R_F2 = 0.061$, $R_F = 0.036$. The structure is built from corner-linked $[PbO_4]$ polyhedra, containing a lone pair of electrons. These polyhedra are connected to layers by phosphonate groups, RPO_3^{2-} and through the organic diphosphonic acid to a three-dimensional structure. Thermogravimetric as well as IR spectroscopic studies are also presented.

Keywords: Lead; Phosphonate; Hybrid material; Hydrothermal synthesis; IR spectroscopy; X-ray diffraction; Rietveld refinement

1. Introduction

Open-framework hybrid materials with organic and inorganic moieties are an attractive field of research due to their composite properties and the possibility of tuning their chemistry [1]. The potential of these inorganic–organic hybrid materials lies in their use as sorbents, ion exchangers, catalysts or charge storage materials. The use of bifunctional anionic units in this field [2], e.g. diphosphonates ($[O_3P–R–PO_3]^{4-}$) [3], aminophosphonates ($[O_3P–R–NH_2]^{2-}$) [4], and phosphonocarboxylates ($[O_3P–R–COO]^{3-}$) [5], has led to many new three-dimensional compounds of di-, tri-, and tetra-valent metals. The layered structures formed by many of these compounds are particularly interesting [3]. The synthesis of phosphonate-based inorganic–organic hybrid materials is generally achieved by using phosphonic acids. Only recently the application of phosphonate esters as a starting material and the advantage in the synthesis of more crystalline Zr(IV) phosphonate materials has been demonstrated [6]. Whereas a vast number of organic–inorganic hybrid materials with many metals have been described, little is known about the corresponding lead(II) compounds. Pb^{2+} has a lone pair of electrons and could therefore lead to interesting topological arrangements or to materials with redox as well as catalytic properties. In the literature only the following materials have been described: $Pb(HO_3PC_6H_5)_2$ [7], $Pb[C(CH_3)(OH)(PO_3H)_2]$ [8], three lead triphosphonates based on nitrilotris(methylene)-triphosphonic acid ($Pb[(H_2O_3PCH_2)N(CH_2PO_3H)_2]$, $Pb_2[(O_3PCH_2)N(CH_2PO_3H)_2] \cdot H_2O$, $Pb_2[(O_3PCH_2)N(CH_2PO_3H)_2]$) [9] and $Pb_3(O_2CCH_2CH_2PO_3)_2$ which adopts a three-dimensional open-framework structure with several types of channels [10]. Based on the last example, we have investigated the influence of the organic unit R as well as the exchange of the carboxylic by a phosphonate group by using instead of phosphonopropionic acid, $HO_2CCH_2CH_2PO_3H_2$, phosphonomethyl-amino acetic acid, $HO_2CCH_2NHCH_2PO_3H_2$, and imino-bis(methylphosphonic) acid, $H_2O_3PCH_2NHCH_2PO_3H_2$ with the goal to obtain materials with larger channels [11]. The resulting materials $Pb(HO_3PCH_2NHCH_2PO_3H)$ and $HPb(O_3PCH_2NHCH_2COO)$ have a three-dimensional framework structure and a layered structure, respectively.

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Recently, we have started a systematic investigation of metal diphosphonates using the α,α′-p-xylenediphosphonic acid and the corresponding tetraethyl α,α′-p-xylenediphosphonate as starting materials [12,13]. These studies have led to the formation of the diphosphonates $M_2^{II}(O_3PCH_2C_6H_4CH_2PO_3)\cdot 2H_2O$ [12] with M = Mn, Ni, Cd and $Sn_2(O_3PCH_2C_6H_4CH_2PO_3)$ [13]. Furthermore, the copper diphosphonate $Cu_2(O_3PCH_2C_6H_4CH_2PO_3)\cdot 2H_2O$ has been reported in the literature [14]. We report here the synthesis of a new lead diphosphonate using tetraethyl α,α′-p-xylene-diphosphonate, $Et_2O_3PCH_2C_6H_4CH_2PO_3Et_2$, and its characterization by ab inito structure determination by X-ray powder diffraction, thermal analysis and IR spectroscopy.

2. Experimental

2.1. Synthesis

The tetraethyldiphosphonate was synthesized by a classical Arbuzov reaction [15]. $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$ was obtained by dissolving 82.8 mg (0.25 mmol) of $Pb(NO_3)_2$ (Merck) in 7.5 g water and adding 66.5 mg (0.18 mmol) $Et_2O_3PCH_2C_6H_4CH_2PO_3Et_2$ under stirring. The reaction mixture was stirred to homogeneity, transferred to a 23 mL PTFE bottle and sealed in a stainless-steel autoclave (Parr, USA). The reaction was carried out at 160°C for 48 h under autogeneous pressure. The resulting single-phase product was filtered and washed thoroughly with deionized water (yield: ~60%).

2.2. Physical characterization

IR spectra were recorded on a Bruker IFS 66v/S FTIR spectrometer in the spectral range 4000–400 cm^{-1} using the KBr disk method. Thermogravimetric analysis was performed on a simultaneous thermal analyzer Netzsch STA 409 under air (40 $cm^3\,min^{-1}$, heating rate 10°C min^{-1}) performing TG and DTA/DSC measurements.

2.3. X-ray structure determination

As no suitable single crystal was obtained a structure determination from X-ray powder diffraction data was performed. The powder was enclosed in a glass capillary (diameter 0.3 mm) and a powder diffraction pattern was measured with a STOE Stadi P diffractometer in Debye–Scherrer geometry. Because of the high absorption coefficient of lead monochromated Mo$K\alpha_1$ radiation was used.

The obtained powder pattern was indexed by the program ITO [16] with a monoclinic cell. The systematic absences are consistent with the space group $P2_1/c$. By comparison of the cell volume with that of other diphosphonates two formula units per cell were assumed. Structure determination by direct methods using the programs EXTRA [17] and SIRPOW [18] only revealed the positions of Pb and P with enough certainty. With this information a Rietveld refinement by the program GSAS [19] was carried out. Successive difference Fourier maps revealed the positions of all O and C atoms. The following Rietveld refinement of the structure converged to satisfactory agreement factors. Although the interatomic distances are not as accurate as with single-crystal data, no restraints of the distances were necessary to obtain a chemically reasonable structure. The thermal displacement factors of all atoms were constrained to be equal. A final difference Fourier map revealed no further electron density caused by possible additional oxygen atoms of water molecules as found in other diphosphonate compounds. The observed and calculated X-ray powder diffraction pattern as well as the difference profile of the Rietveld refinement of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$ are shown in Fig. 1. Detailed crystallographic data are summarized in Table 1, the refined atomic parameters are listed in Table 2. Table 3 gives selected interatomic distances and angles.

3. Results and discussion

3.1. Synthesis

The use of alkylphosphonates instead of phosphonic acids in the synthesis of inorganic–organic hybrid materials so far has received little attention. Thus only recently the use of dialkylphosphonates in the synthesis of zirconium phosphonate materials under aqueous

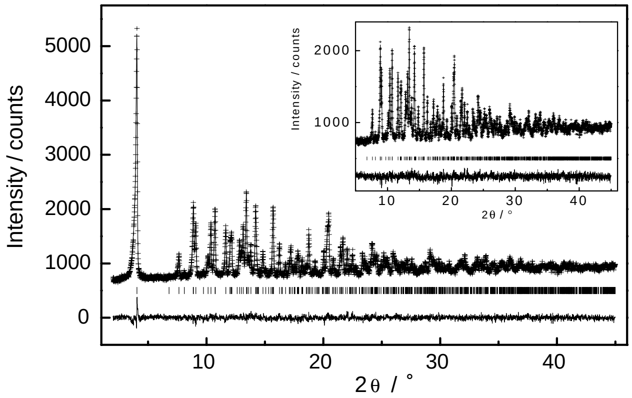

Fig. 1. Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as difference profile of the Rietveld refinement of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$ (STOE Stadi P, $\lambda = 70.930$ pm). The row of vertical lines indicates possible peak positions.

Table 1
Crystallographic data for $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$

Formula	$Pb_2P_2C_8O_6H_8$
Formula weight	676.46
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Lattice parameters /pm,/deg	$a = 467.84(2)$ $b = 2007.98(9)$ $c = 639.10(2)$ $\beta = 101.020(3)$
Volume/$10^6\,pm^3$	589.31(4)
Z	2
$\rho_c/g\,cm^{-3}$	3.812
Radiation (λ/pm)	$MoK\alpha_1$ (70.93)
Profile range	$2^\circ \leqslant 2\theta \leqslant 45^\circ$
No. data points	4300
No. reflections	767
Positional param.	28
Profile param.	17
R-values	$wR_p = 0.034$, $R_p = 0.027$ $R_F2 = 0.061$, $R_F = 0.036$

Table 2
Atomic coordinates and displacement factors (pm^2) of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$

Atom	Wyckoff position	x	y	z	U_{iso}[a]
Pb	4c	0.8135(4)	0.3075(1)	0.1720(3)	74(3)
P	4c	0.265(3)	0.1728(6)	0.266(2)	74(3)
O1	4c	0.060(5)	0.208(1)	0.106(4)	74(3)
O2	4c	0.173(5)	0.151(1)	0.479(4)	74(3)
O3	4c	0.518(5)	0.221(1)	0.339(4)	74(3)
C1	4c	0.462(8)	0.106(2)	0.138(6)	74(3)
C2	4c	0.241(9)	0.057(2)	0.082(6)	74(3)
C3	4c	0.113(9)	0.010(2)	0.210(6)	74(3)
C4	4c	0.106(9)	0.040(2)	−0.144(7)	74(3)

[a] U_{iso} is defined as exp $(-8\pi^2 U_{iso}\sin^2\theta/\lambda^2)$, the displacement factors of all atoms are constrained to be equal.

Table 3
Bond distances (pm) and angles (deg) in $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$

Pb–O1	239(3)	O1–Pb–O2	78.2(9)
Pb–O2	242(2)	O1–Pb–O3	79.9(9)
Pb–O3	257(2)	O1–Pb–O3	81.7(8)
Pb–O3	238(2)	O2–Pb–O3	158.0(7)
		O2–Pb–O3	88.2(7)
		O3–Pb–O3	86.7(6)
P–O1	144(2)	O1–P–O2	120(2)
P–O2	157(2)	O1–P–O3	106(1)
P–O3	154(3)	O1–P–C1	111(2)
P–C1	190(3)	O2–P–O3	104(2)
		O2–P–C1	114(2)
		O3–P–C1	100(2)
C1–C2	142(5)	P–C1–C2	102(3)
C2–C3	145(5)	C1–C2–C3	132(4)
C2–C4	150(5)	C1–C2–C4	124(4)
C3–C4	144(5)	C3–C2–C4	104(4)
		C2–C3–C4	130(4)
		C2–C4–C3	126(4)

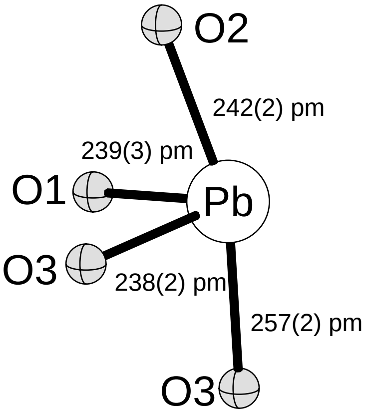

Fig. 2. Coordination of Pb^{2+} in $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$.

acidic conditions (HCl) has been shown to yield crystalline materials [6]. Due to the slow hydrolysis of the dialkylphosphonate more crystalline products were obtained. Our use of tetraalkylphosphonates in the synthesis of metal(II) phosphonates has led to the synthesis of microcrystalline $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$. In contrast to the previous study no additional acid was required. The approach of using alkylphosphonates instead of the phosphonic acid has the advantage that pure alkylphosphonates can readily be obtained by chromatography, recrystallization or distillation. Phosphonic acids on the other hand are hard to purify.

3.2. X-ray crystal structure

The crystal structure of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$ contains trigonal bipyramidal $[PbO_4]$ polyhedra (the lone pair occupying the fifth coordination site) (Fig. 2). These polyhedra are corner-linked and form chains along [001]. The RPO_3 units of the diphosphonic acid connect the PbO chains to layers in the (010) plane (Fig. 3). These inorganic layers are at $y \backsim \frac{1}{4}$ and $\backsim \frac{3}{4}$ and are pillared by the $–CH_2C_6H_4CH_2–$ units thus forming a three-dimensional structure (Figs. 4 and 5). The center of gravity of the organic units are located at $y \sim 0$ and $\backsim \frac{1}{2}$. Due to the presence of the $–CH_2–$ groups the phenyl rings are tilted by 40(1)° with respect to the normal of the layer plane. They are parallel to each other in the same layer, but between two layers the dihedral angle between the least-square planes of the phenyl rings is approximately 80°. Thus a ABAB-type stacking of the pillars is observed. This is in contrast to the findings in $M_2(O_3PCH_2C_6H_4CH_2PO_3)\cdot 2H_2O$ (M = Mn, Ni, Cd) [12] and $Cu_2(O_3PCH_2C_6H_4CH_2PO_3)\cdot 2H_2O$ [14] where a substantially different arrangement of the phenyl rings is observed. In the copper compound, the least-square planes of the phenyl rings in one layer are slightly tilted to each other and form a AAAA-type stacking [14]. In

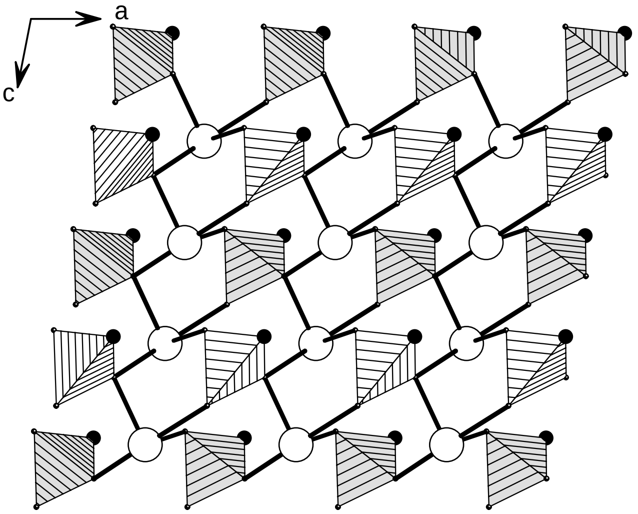

Fig. 3. Corner-linked [PbO_4] polyhedra form chains along [0 0 1] which are connected to layers in the (010) plane by the phosphonate groups RPO_3^{2-}. View along [010].

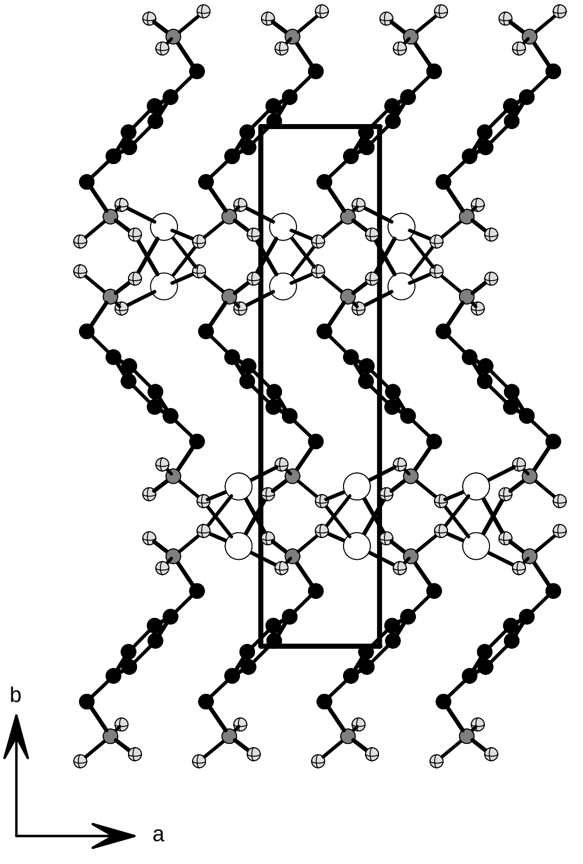

Fig. 4. Pillared structure of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$. View along [001].

the Mn, Ni and Cd compound the least-square planes of the phenyl rings in one layer are strongly tilted to each other and show a ABAB-type stacking [12].

In comparison to other metal $\alpha,\alpha' - p$-xylenediphosphonates the title compound exhibits a different M–O layer structure, which has not been observed previously in other lead phosphonates. The layers in $M_2(O_3PCH_2C_6H_4CH_2PO_3) \cdot 2H_2O$ (M = Mn, Ni, Cd) [12] are composed of corner-linked [$MO_5(H_2O)$] polyhedra and in $Cu_2(O_3PCH_2C_6H_4CH_2PO_3) \cdot 2H_2O$ dimers of edge-sharing [$CuO_4(H_2O)$] square pyramids are observed [14]. Both types of layer structures have been previously encountered in the layered structure of the corresponding phenylphosphonates [20,21].

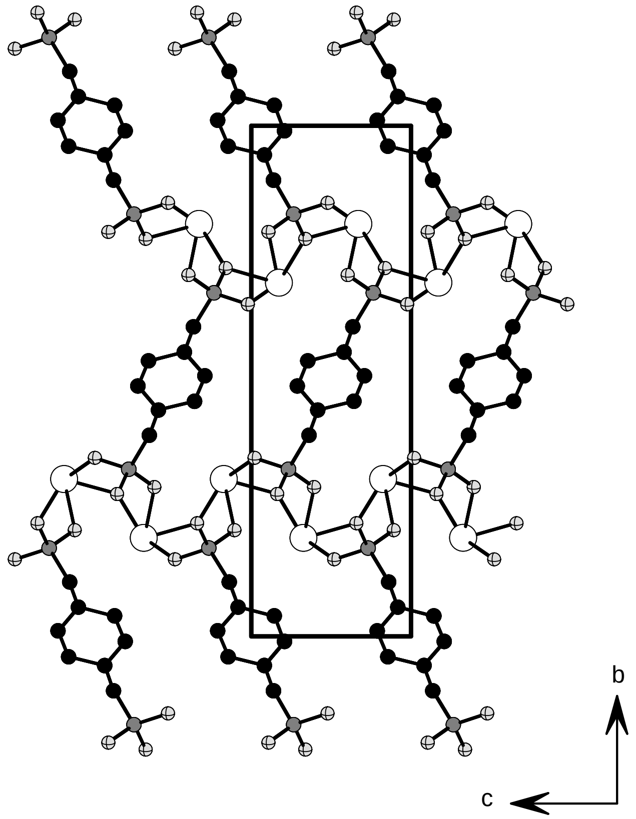

Fig. 5. Pillared structure of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$. View along [100].

3.3. IR spectroscopy

The absence of water in the title compound was confirmed by the absence of a band between 3400 and 3500 cm^{-1} in the IR spectrum. Therefore, only the relevant part of the IR spectrum of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$ is shown in Fig. 6. The spectrum is similar to the ones observed for $M_2(O_3PCH_2C_6H_4CH_2PO_3) \cdot 2H_2O$ (M = Mn, Ni, Cd) [12]. The small band at 3051 cm^{-1} and the more intensive band 3026 cm^{-1} are characteristic of the C–H stretching vibration of the phenyl ring and the bands between 2933 and 2895 cm^{-1} can be attributed to the asymmetric and symmetric C–H stretching vibrations of the –CH_2 groups, respectively (inset Fig. 6). The IR spectrum is typical for a para-substituted

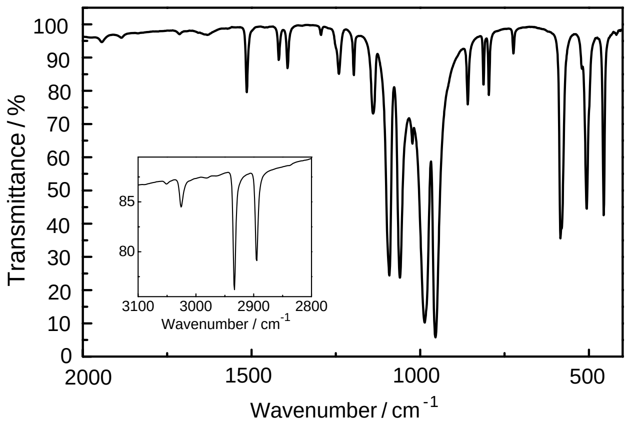

Fig. 6. IR spectrum of $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$.

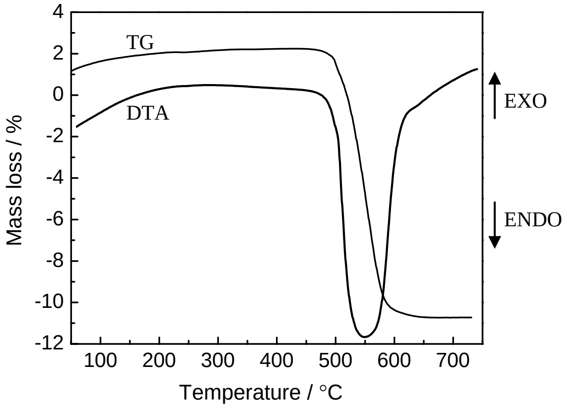

Fig. 7. TG-DTA curves for $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$.

benzene ring [22]. As observed in α,α'dibromo *p*-xylene, three skeletal ring vibration modes at 1514, 1419 and 1393 cm^{-1} can be found. As expected for para-substituted benzene rings, one sharp δ CH out-of-plane vibration at 859.1 cm^{-1} and three overtone and combination bands are found in the region between 2000 and 1650 cm^{-1} (at 1944, 1886, 1713 cm^{-1}). The set of bands between 1200 and 900 cm^{-1} (954, 986, 1061, 1092 cm^{-1}) are assigned to stretching vibrations of the tetrahedral CPO_3 groups. Additional intensive and sharp bands at low energy (456, 506, 584 cm^{-1}) are found. These bands are probably due to bending vibrations of the tetrahedral CPO_3 groups and Pb–O stretching vibrations.

3.4. Thermal study

The TG-DTA curve for $Pb_2(O_3PCH_2C_6H_4CH_2PO_3)$ is shown in Fig. 7. The DTA curve shows one endothermic signal, which is due to the pyrolysis of the organic matter. The TG curve confirms the absence of crystal water. Only one weight loss of 13.0% between 440°C and 650°C is observed which is due to the decomposition of the title compound under formation of $Pb_2P_2O_7$ (theory 13.1%, Eq. (1); confirmed with X-ray powder diffraction).

$$Pb_2(O_3PCH_2C_6H_4CH_2PO_3) + 7O_2(g) \rightarrow Pb_2P_2O_7 + 8CO_2(g) + 4H_2O(g).$$

This result is also in agreement with the thermal study of $Pb_2[(O_3PCH_2)N(CH_2PO_3H)_2] \cdot H_2O$ that showed the formation of $Pb_2P_2O_7$ [9].

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