

X-Ray Diffraction and Infrared Spectroscopy Data Review Analyses of the Calcium Phosphates

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Abstract: The objective of this literature reviews is to report the various methods used in the synthesis of the calcium monophosphates and condensed phosphates compounds, such as the co-precipitation method, Boule's process, solid-state reactions, hydrothermal synthesis, and thermal dehydration, and present the crystalline data of these salts as classified from the hexagonal to the triclinic system. For the monophosphates, the compounds with $(\text{PO}_4)^{3-}$ groups crystallized in the hexagonal, rhombohedral, trigonal, orthorhombic, and monoclinic systems, against the compounds with $(\text{HPO}_4)^{2-}$ and $(\text{H}_2\text{PO}_4)^{-}$, which are crystallized in low symmetry systems (monoclinic, and triclinic). For the long polyphosphates chain $(\text{PO}_3)_n$, where the formula contains one $(\text{PO}_4)^{3-}$ group, the compounds crystallized in the high possible symmetry (tetragonal systems); the compounds of a formula containing two, three, and four $(\text{PO}_4)^{3-}$ groups are crystallized in the lower symmetry systems (monoclinic, and triclinic). In the anhydrous cyclotetraphosphates, the substitution of 2K^+ by Ca^{2+} induced lowering symmetry from the tetragonal system in $\text{CaK}_2\text{P}_4\text{O}_{12}$ to the triclinic system in $\text{Ca}_2\text{P}_4\text{O}_{12}$. The calcium cyclohexaphosphates are all found to be hydrate compounds. With ammonium cations, the $(\text{NH}_4)_6\text{P}_6\text{O}_{18} \cdot 1.5\text{H}_2\text{O}$ crystallized in the orthorhombic system, as a highly symmetrical system found in this phosphate type. Besides, the study is extended to review the inferred characterization made particularly for anions, PO_3^{3-} in $\gamma\text{-Ca}(\text{PO}_3)_2$, PO_4^{3-} in CaHPO_4 , $\text{P}_2\text{O}_7^{4-}$ in $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, $\text{P}_3\text{O}_9^{3-}$ in $\text{MnCa}_2(\text{P}_3\text{O}_9)_2$, $\text{P}_4\text{O}_{12}^{4-}$ in $\text{Ca}_2\text{P}_4\text{O}_{12} \cdot 1.5\text{H}_2\text{O} \cdot 3\text{H}_2\text{O}$ and $\text{P}_6\text{O}_{18}^{6-}$ in $\text{Ca}_2\text{K}_2\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$.

Keywords: chemical synthesis; X-ray diffraction; infrared vibration; condensed phosphate; monophosphate; calcium.

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1. Introduction

Materials based on monophosphates and condensed phosphates associated with calcium (Ca-P) have been developed considerably during recent decades. These compounds are found to be interesting in many fields of applications such as bioactive ceramics, biology, building materials (cement), and biotechnological materials [1-4]. For this reason, several review articles were interested in calcium phosphate [5,6]. On the other hand, the chemical synthesis, crystalline data, and infrared spectroscopy of some characteristic anions of monophosphates and condensed phosphates associated with some alkaline earth elements [$\text{M}^{\text{II}}=\text{Ba}, \text{Sr}$] [7,8] and transition elements [$\text{M}=\text{Mn}$] [9] have been recently reviewed.

In the present work, we will develop a review study to report and analyses the synthesis, X-ray, and infrared characteristics of monophosphates and condensed phosphates associated with calcium (Ca-P).

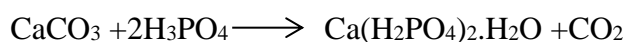
2. Monophosphates PO_4^{3-}

2.1. Synthesis.

In this part, we present the synthesis details of monophosphate associated with calcium, which has been prepared by various synthetic methods, such as: the co-precipitation method, hydrothermal synthesis, and thermal method.

2.1.1. $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

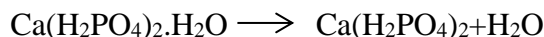
This compound was prepared by Bac *et al.* [10] by solution precipitation methods using calcium carbonate CaCO_3 and phosphoric acid H_3PO_4 as starting materials. In a typical procedure, 23g of H_3PO_4 was diluted with 14g of water, and then the formed solution was heated to 90°C in a water bath. Calcium carbonate CaCO_3 was then gradually added in small portions, according to the following chemical reaction:



The so-obtained solution was stirred continuously for c.a. 1 hour to form a homogeneous mixture. The product was dried at 95°C and obtained 25 g white powder.

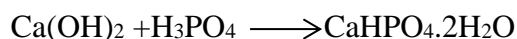
2.1.2. $\text{Ca}(\text{H}_2\text{PO}_4)_2$

This anhydrous compound was obtained by Bac *et al.* [10,11] by thermal dehydration of the hydrated phase $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at 120°C , according to the following chemical reaction:



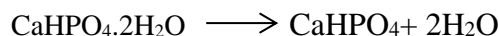
2.1.3. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

The titled crystal was prepared by Curry *et al.* [12] by neutralization of phosphoric acid H_3PO_4 with calcium hydroxide $\text{Ca}(\text{OH})_2$ at pH between 3 and 4, and at room temperature, according to the following chemical reaction:



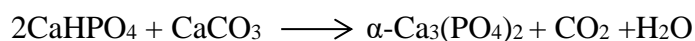
2.1.4. CaHPO_4 .

This anhydrous compound was obtained by Dickens *et al.* [13] by thermal dehydration of the hydrated phase $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at 180°C , according to the following chemical reaction:



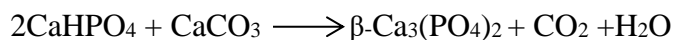
2.1.5. $\alpha\text{-Ca}_3(\text{PO}_4)_2$.

Samples of $\alpha\text{-Ca}_3(\text{PO}_4)_2$ were prepared by Mathew *et al.* [14] by heating pressed pellets of stoichiometric amounts of CaHPO_4 and calcium carbonate CaCO_3 , mixed with 1% cornstarch and a few drops of distilled water, to 1400°C for two days, like the following:



2.1.6. β -Ca₃(PO₄)₂.

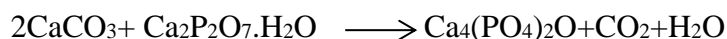
Yashima *et al.* [15] have prepared the titled compound by solid-state reactions from CaHPO₄ and CaCO₃. Stoichiometric amounts of CaHPO₄ and calcium carbonate CaCO₃ were mixed for about 1.5h in an agate mortar, like the following:



The mixture was pressed into pellets under uniaxial pressure of 150 MPa. The pellets were sintered for 24h at 1000 °C to obtain a single phase of β -Ca₃(PO₄)₂.

2.1.7. Ca₄(PO₄)₂O.

This phase was obtained by Dickens *et al.* [16] by heating at high temperature a mixture of calcium carbonate CaCO₃ and phosphate salts Ca₂P₂O₇.H₂O with a Ca/P ratio close to 2, according to the following chemical reaction:



2.1.8. Ca₁₀(PO₄)₆F₂.

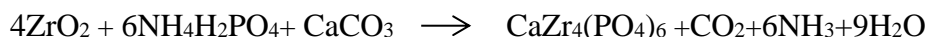
This compound was prepared by Abrouki *et al.* [17] by the co-precipitation method using diammonium phosphate (NH₄)₂HPO₄, calcium nitrate Ca(NO₃)₂ and ammonium fluoride NH₄F as starting materials. In a typical procedure, 250 mL of a solution containing 7.92 g of (NH₄)₂HPO₄ and 1 g of NH₄F, maintained at pH greater than 12 by addition of ammonium hydroxide (15-20 mL), were dropped under constant stirring into 150 mL of a solution containing 23.6 g calcium nitrate (Ca(NO₃)₂·4H₂O), according to the following chemical reaction.



The obtained product was filtered, washed with doubly distilled water, dried overnight at 80°C, and calcined in air at 700°C.

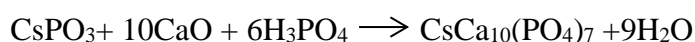
2.1.9. CaZr₄(PO₄)₆.

Powder crystalline of CaZr₄(PO₄)₆ have been prepared by Alamo *et al.* [18] from mixtures of ZrO₂, NH₄H₂PO₄, and CaCO₃ in stoichiometric proportions and heated in three steps at 800°C for 12 h, at 1200°C for 12 h and at 1300°C for 10 h to obtain a single-phase, according to the following chemical reaction:



2.1.10. CsCa₁₀(PO₄)₇ and Cs_{0.63}Ca_{9.63}Fe_{0.37}(PO₄)₇.

The two compounds were prepared by Zatovsky *et al.* [19] by solid-state reactions from CsPO₃, CaO, and Fe₂O₃. The calculated amounts of CsPO₃, CaO, and Fe₂O₃ were ground, put into a platinum crucible, and the necessary amount of H₃PO₄ was added to the mixture, following this chemical reaction:

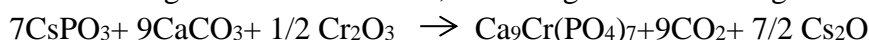




The crucibles were put into the cold furnace and slowly heated up to 1073 K. At this temperature, the flux was exposed during 40-50 min to reach homogeneity. The crystallization was performed at a rate of 30–50 K/h down to 943-923 K.

2.1.11. $\text{Ca}_9\text{Cr}(\text{PO}_4)_7$.

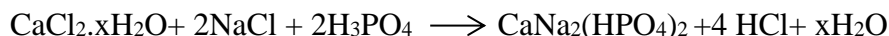
This compound was prepared by Zatovsky *et al.* [20] by solid-state reaction methods using CsPO_3 , CaCO_3 , and Cr_2O_3 as starting materials. In a typical procedure, a mixture of CsPO_3 , CaCO_3 , and Cr_2O_3 was ground in an agate mortar, placed into a platinum crucible, and heated up to 1273 K. The melt was kept at this temperature until it became homogenous (2h). The temperature was then decreased to 1053 K at a rate of 30 K h⁻¹, and at this temperature, the remaining flux was decanted, according to the following chemical reactions:



The crucible was cooled down to room temperature. The solidified melt was leached out with deionized water, and light-green crystals of $\text{Ca}_9\text{Cr}(\text{PO}_4)_7$ were recovered.

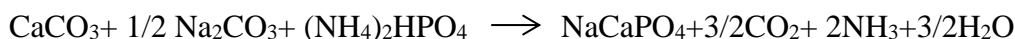
2.1.12. $\text{CaNa}_2(\text{HPO}_4)_2$.

This compound was prepared by Ben Chaabane *et al.* [21] by hydrothermal synthesis using $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$, NaCl , H_3PO_4 , and $\text{C}_6\text{H}_{15}\text{N}$ as starting materials. A mixture of $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$ (805 mg), NaCl (847 mg), H_3PO_4 (14.4 mmol), and $\text{C}_6\text{H}_{15}\text{N}$ (24.6 mmol) was placed in a Teflon vessel and filled to a degree of 80% with water (final pH = 9.5). The obtained product was heated at 180°C for 5 days, and the powder compound $\text{CaNa}_2(\text{HPO}_4)_2$ was recovered by vacuum filtration and air drying, according to the following chemical reactions:



2.1.13. NaCaPO_4 .

This compound was prepared by Ben Amara *et al.* [22] from a stoichiometric mixture of sodium carbonate Na_2CO_3 , calcium carbonate CaCO_3 and ammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$, according to the following chemical reactions:



The initial mixture was first heated at 673 K under a nitrogen stream, then at 1223 K in air. Single crystals of NaCaPO_4 were grown by cooling, from 1073 to 473 K at a rate of 10 K h⁻¹.

2.2. Crystallographic data.

In this part, we reported the main crystallographic data for the various monophosphates associated with calcium, classified from the hexagonal to the triclinic system (Table 1).

Compound	System	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	Hexagonal	P6 ₃ /m	1	9.364	9.364	6.893	[17]
$\text{CaZr}_4(\text{PO}_4)_6$		R-3		8.7859	8.7852	22.6620	[18]
β $\text{Ca}_3(\text{PO}_4)_2$	Rhombohedral	R3c	21	10.4352	10.4352	37.4029	[15]

Compound	System	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
	(hexagonal setting)						
CsCa ₁₀ (PO ₄) ₇	Trigonal	R3c	6	10.5536	10.5536	37.2283	[19]
Cs _{0.63} Ca _{9.63} Fe _{0.37} (PO ₄) ₇		R3c	6	10.5221	10.5221	37.2405	[19]
Ca ₉ Cr(PO ₄) ₇		R3c	6	10.3272	10.3272	37.132	[20]
NaCaPO ₄	Orthorhombic	Pn2 ₁ a	12	20.397	5.412	9.161	[22]
CaHPO ₄ ·2H ₂ O	Monoclinic	Ia(C _s ⁴)	4	5.812	15.180 116.25	6.239	[12]
α Ca ₃ (PO ₄) ₂		P2 ₁ /a	24	12.887	27.280 126.20	15.219	[14]
Ca ₄ (PO ₄) ₂ O		P2 ₁	4	7.023	11.986 90,90	9.473	[16]
CaNa ₂ (HPO ₄) ₂		P2 ₁	2	9.0652	7.1468 98.782	5.4700	[21]
Ca(H ₂ PO ₄) ₂ ·H ₂ O	Triclinic	P-1	2	5.6125 98.3516	11.8821 117.7303	6.4324 83.5106	[10]
Ca(H ₂ PO ₄) ₂		P-1	2	7.5577 109.87	8.2531 93.68	5.5504 109.15	[10,11]
CaHPO ₄		P-1	4	6.910 96.34	6.627 103.82	6.998 88.33	[13]

Table 1. Main crystallographic data for the monophosphates associated with calcium, classified from the hexagonal to the triclinic system.

It is worthy to note that the compounds containing the (PO₄)³⁻ groups are crystallizing in the hexagonal, rhombohedral, trigonal, orthorhombic, and monoclinic systems, against the compound with (HPO₄)²⁻ and (H₂PO₄)⁻, which crystallized in the systems with low symmetry (monoclinic, and triclinic).

2.3. Infrared characterization studies made on PO₄³⁻ in the monetite, CaHPO₄.

Tortet *et al.* [23] have studied the infrared spectrum of monetite, CaHPO₄ at 25°C. In this study, the infrared stretching ν (OH) observed at 3190, 2849, and 2360 cm⁻¹ was found to be strongly dependent on hydrogen bonding taken place in this compound. The broad band that appeared in 1450-1300 cm⁻¹ was assigned to the P—O—H in-plane bending. The P—O and P—O(H) stretching of the phosphate [PO₄]³⁻ anion [24-26] were assigned to the features observed as strong and medium absorptions bands at 1081 cm⁻¹ and 891 cm⁻¹ in the IR spectrum. The O—P—O (H) and O—P—O vibrations of the phosphate [PO₄]³⁻ anion appeared at 578 cm⁻¹ and 420 cm⁻¹, respectively (Table 2).

Table 2. Frequencies (cm⁻¹) of IR absorption bands for monetite, CaHPO₄.

Infrared (ν /cm ⁻¹)	Assignments [23-26]
3447	O—H stretching of residual free water
3190 ; 2849 ; 2360	(P)O—H stretching modes
1600—1700 (broad)	H—O—H bending and rotation of residual free water
1450—1300 (broad)	P—O—H in-plane bending
1170; 1131 ; 1081	P—O stretching modes
996	P—O stretching modes
891	P—O(H) stretching
578	O—P—O(H)
532	bending modes
420	O—P—O
404	bending modes

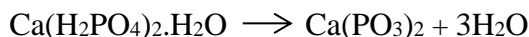
3. Long polyphosphates chain (PO₃⁻)_n

3.1. Synthesis.

The polyphosphates associated with calcium were prepared by various synthetic methods, such as the conventional solid-state method and thermic method.

3.1.1. Ca(PO₃)₂

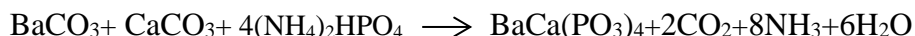
This compound was prepared by Rothammel *et al.* [27] by thermal dehydration of the hydrated phase Ca(H₂PO₄)₂.H₂O at 1523 K, according to the following chemical reactions:



Cooling of the melt to 1223 K gives crystals of Ca(PO₃)₂ sufficiently large and high quality.

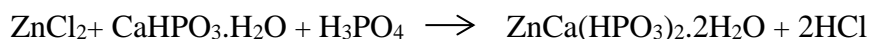
3.1.2. BaCa(PO₃)₄.

This salt was prepared by Averbuch-Pouchot [28] by calcination at 700°C of a mixture in stoichiometric proportions of diammonium monophosphate (NH₄)₂HPO₄, barium carbonate BaCO₃ and calcium carbonate CaCO₃, according to the following chemical reactions:



3.1.3. ZnCa(HPO₃)₂.2H₂O.

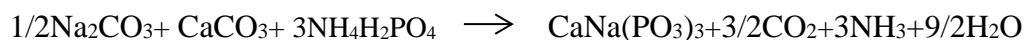
The titled compound was prepared by Shieh *et al.* [29], by solution precipitation methods using ZnCl₂, CaHPO₃.H₂O, and phosphoric acid H₃PO₄ as starting materials. 0.67 g of ZnCl₂, was added to a solution of 1.20 g of CaHPO₃.H₂O in 10 mL of aqueous 1M H₃PO₃, according to the following chemical reactions:



The clear solution was stirred overnight, followed by the addition of 7 mL of EtOH. Colorless platelike crystals were obtained after the solution had been allowed to stand for several days at room temperature.

3.1.4. CaNa(PO₃)₃.

This compound was prepared by Abrahams *et al.* [30] by the conventional solid-state method. Appropriate stoichiometric amounts of Na₂CO₃, NH₄H₂PO₄, and CaCO₃ were milled; the dried mixture was placed in a platinum crucible and heated at 300 °C. For 1 hour to decompose the carbonate and then heated for 12 hours at 700 °C, according to the following chemical reactions:

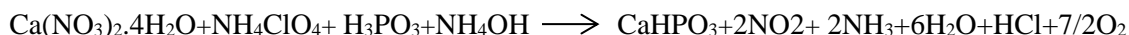


The crystalline materials of CaNa(PO₃)₃ were obtained by quench quenching to the air.

3.1.5. CaHPO₃.

Using Ca(NO₃)₂.4H₂O and phosphorous acid H₃PO₃(as starting materials), Phillips *et al.* [31] have prepared the above-mentioned compound. A mixture of 0.52 g of H₃PO₃, 2.36 g

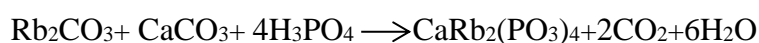
of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and 0.47 g of NH_4ClO_4 was dissolved in 10 ml of H_2O , then mixed with 4.0 g of 15 N NH_4OH and loaded into a 23 ml Teflon cup, according to the following chemical reactions:



The reaction mixture was heated in a pressure vessel for seven days at 473 K and cooled to room temperature for a few hours. The product of CaHPO_3 was recovered by vacuum filtration and rinsed with deionized water.

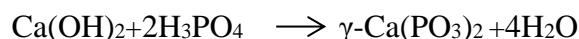
3.1.6. $\text{CaRb}_2(\text{PO}_3)_4$.

This crystal was prepared by Henry *et al.* [32] by calcining of a mixture of equimolecular rubidium Rb_2CO_3 and calcium CaCO_3 carbonates in a large excess of orthophosphoric acid H_3PO_4 at 400 °C for 24 hours, as the following chemical reactions:



3.1.7. $\gamma\text{-Ca}(\text{PO}_3)_2$.

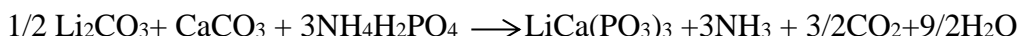
This compound was synthesized by Jackson *et al.* [33] from an acidic flux containing calcium hydroxide $\text{Ca}(\text{OH})_2$ and phosphoric acid H_3PO_4 , according to the following chemical reactions:



The reaction mixture was heated to 250 °C for 24 hours and allowed to cool. The final products were collected by filtration and washed and then left to dry for 2-3 hours at 120 °C.

3.1.8. $\text{LiCa}(\text{PO}_3)_3$.

This crystal was prepared by Han *et al.* [34] by the conventional solid-state method. Appropriate stoichiometric amounts of Li_2CO_3 , CaCO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were milled; the dried mixture was placed in a platinum crucible and heated at 650 °C and held at this temperature for 5 h to obtain a transparent solution, according to the following chemical reactions:



The solution was quickly cooled to 590 °C and then the temperature lowered to 350 °C at a rate of 2 °C h⁻¹. After this process, it was cooled down to room temperature at a rate of 15 °C h⁻¹. During the slow cooling process, some crystals were obtained.

3.2. Crystallographic data.

In this part, we reported the main crystallographic data for the various polyphosphate associated with calcium, classified from the hexagonal to the triclinic system (Table 3).

Table 3. Main crystallographic data for the polyphosphates associated with calcium, classified from the hexagonal to the triclinic system.

Compound	system	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
CaHPO_3	Tetragonal	P4_32_12	8	6.67496	6.67496	12.9542	[31]
$\text{Ca}(\text{PO}_3)_2$	Monoclinic	$\text{P2}_1/\text{a}$	8	16.960	7.7144 90.394	6.9963	[27]
$\text{BaCa}(\text{PO}_3)_4$		$\text{P2}_1/\text{n}$	4	15.24	9.173	7.231	[28]

Compound	system	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
					90.96		
CaRb ₂ (PO ₃) ₄		P2 ₁ /n	4	11.436	13.352 101.89	7.908	[32]
ZnCa(HPO ₃) ₂ ·2H ₂ O		P2 ₁ /n	4	7.131	7.766 97.30	14.479	[29]
γCa(PO ₃) ₂		Cc	8	9.5669	9.5023 93.474	10.3717	[33]
CaNa(PO ₃) ₃	Triclinic	P-1	2	6.711 83.44	6.934 81.41	7.619 82.80	[30]
LiCa(PO ₃) ₃		P-1	2	6.6726 83.839	6.9181 80.595	7.334 81.797	[34]

For the long polyphosphates chain (PO₃⁻)_n, one can state that when the formula contains one (PO₄)³⁻ group, the corresponding compound is crystallizing in the high symmetry (tetragonal systems), the compounds belonging to the formula with two, three, and four (PO₄)³⁻ groups are crystallized in the systems with lower symmetry (monoclinic, and triclinic).

3.3. Infrared characterization studies made on PO₃⁻ in γ-Ca(PO₃)₂.

Jackson *et al.* [33] have studied the infrared spectrum of the sample of γ-Ca(PO₃)₂ at room temperature. The band in the region of 850-920 cm⁻¹ was assigned to the antisymmetric stretching vibration of the P-O-P, which is at a low frequency due to the infinite number of PO₄ units. The band in 1160-1170 cm⁻¹ was assigned to the antisymmetric stretching of the terminal PO₃, and the band at 1230-1250 cm⁻¹ to the antisymmetric stretching vibration of the bridging PO₂. The symmetric stretching bridging PO₂ was assigned to the band in 1080-1110 cm⁻¹, and the symmetric PO₃ stretching modes appeared in 940-1020 cm⁻¹ (Table 4).

Table 4. Frequencies (cm⁻¹) of IR absorption bands for γ-Ca(PO₃)₂.

Frequencies (ν /cm ⁻¹)	Assignments[33]
1230-1250	ν _{as} (PO ₂)
1160-1170	ν _{as} (PO ₃)
1080-1110	ν _s (PO ₂)
940-1020	ν _s (PO ₃)
850-920	ν _{as} (P-O-P)

4. Condensed phosphates

4.1. Oligophosphates(P_nO_{3n+1})⁽ⁿ⁺²⁾.

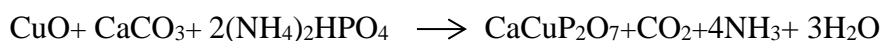
4.1.1. Diphosphates P₂O₇⁴⁻.

4.1.1.1. Synthesis.

In this part, we present the synthesis of the diphosphates associated with calcium by the various synthetic methods: thermic method and co-precipitation method.

4.1.1.1.1. CaCuP₂O₇.

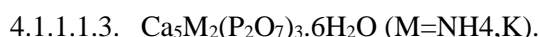
This compound was prepared by Riou *et al.* [35], from a mixture of copper oxide CuO, calcium carbonate CaCO₃ and diammonium phosphate (NH₄)₂HPO₄ in ratios 1:1:2, as the following chemical reaction:



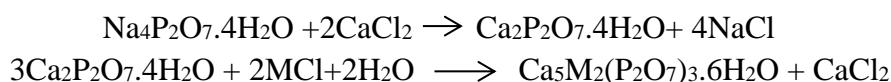
The reaction mixture was first heated at 973 K to decompose the carbonate and the phosphate. The resultant product was ground and heated for nine days at 1333 K. The quenching at room temperature gives crystals of CaCuP_2O_7 sufficiently large and high quality



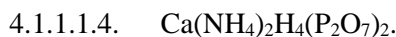
This crystal was prepared by Brown *et al.* [36] by mixing 1 gram of $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ and 15 ml of NH_4OH (0.6M) at room temperature for 24 to 48 hours, according to the following chemical reaction:



These two salts were prepared by Brown *et al.* [36] by adding 1 gram of $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ calcium pyrophosphate (prepared from $\text{Na}_4\text{P}_2\text{O}_7$ and CaCl_2) to a stirred (5M NH_4Cl or 5M KCl) solution at 70° to 75 °C, according to the following chemical reaction:



The products precipitated rapidly. Larger crystals were prepared by allowing a diluted mixture of the reagents to stand at room temperature for about a week.



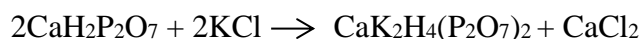
Brown *et al.* [36] have also prepared the $\text{Ca}(\text{NH}_4)_2\text{H}_4(\text{P}_2\text{O}_7)_2$ compound by allowing 5 grams of $\text{CaH}_2\text{P}_2\text{O}_7$ to stand at room temperature in 20 ml of a saturated solution of NH_4Cl for about 24 hours, according to the following chemical reaction:



The product was filtered by suction, suspended in ethyl alcohol to remove NH_4Cl , filtered, rinsed with acetone, and air-dried.



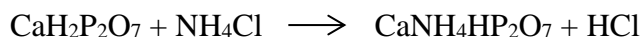
This salt was prepared by Brown *et al.* [36] by adding 5 grams of $\text{CaH}_2\text{P}_2\text{O}_7$ to a mixture of 20 ml of saturated KCl solution and 10 grams of solid KCl and allowing the mixture to stand at room temperature for 12 to 24 hours, according to the following chemical reaction:



The product was filtered rapidly by suction, suspended in ethyl alcohol to remove KCl , filtered, rinsed with acetone, and air-dried.



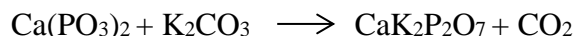
This salt was prepared by Mathew *et al.* [37] by adding 1 g of $\text{CaH}_2\text{P}_2\text{O}_7$ to a solution of 2.4 g of NH_4Cl in 75 ml of H_2O at 65 °C, according to the following chemical reaction:



The solution was allowed to cool to 52 °C over a period of a few hours without stirring. The solution was then held at that temperature overnight to encourage the growth of the title compound.

4.1.1.1.7. $\text{CaK}_2\text{P}_2\text{O}_7$.

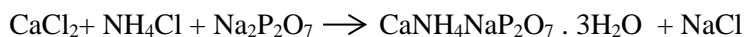
This phase was prepared by Sandström *et al.* [38] by mixing potassium carbonate K_2CO_3 and calcium polyphosphate $\text{Ca}(\text{PO}_3)_2$ at 1273 K in a 1:1 ratio, as illustrated by the following chemical reaction:



Crystals of $\text{CaK}_2\text{P}_2\text{O}_7$ were grown by heating a mixture consisting of $\text{CaK}_2\text{P}_2\text{O}_7$ and KH_2PO_4 at 1323 K for about 12h, followed by cooling at 1023 K, and finally quenching to room temperature. The solidified liquid was crushed, and the resulting colorless crystals were picked out.

4.1.1.1.8. $\text{CaNH}_4\text{NaP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$.

This compound was obtained by Averbuch-Pouchot *et al.* [39] by adding a dilute solution of calcium chloride CaCl_2 to a concentrated solution of ammonium chloride NH_4Cl and sodium diphosphate $\text{Na}_2\text{P}_2\text{O}_7$, which causes the formation of a gel that gradually transforms at room temperature, giving rise to crystals of $\text{CaNH}_4\text{NaP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ sufficiently strong and good quality, according to the following chemical reaction:



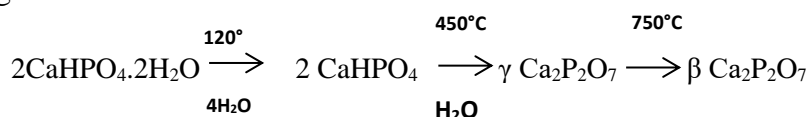
4.1.1.1.9. $\alpha\text{-CaNa}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ and $\beta\text{-CaNa}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$.

The two crystal forms were prepared by Cheng *et al.* [40] by adding 0.1M $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ first neutralized with hydrochloric acid HCl to 1 mM CaCl_2 at room temperature, according to the following chemical reaction:



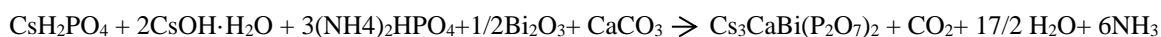
4.1.1.1.10. $\beta\text{-Ca}_2\text{P}_2\text{O}_7$.

This compound was obtained by Webb *et al.* [41,42] by heating the dicalcium phosphate dehydrate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ to approximately 750°C produces $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, as illustrated in the following chemical reaction:



4.1.1.1.11. $\text{Cs}_3\text{CaBi}(\text{P}_2\text{O}_7)_2$.

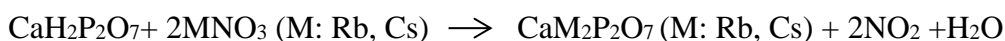
This compound was obtained by Zatovsky *et al.* [43] using the conventional solid-state method. Appropriate stoichiometric amounts of bismuth oxide Bi_2O_3 , calcium CaCO_3 , dihydrogen phosphate CsH_2PO_4 and diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$ were ground and then heated to 1273 K, according to the following chemical reaction:



The molten product was maintained at this temperature for 1 hour, cooled with a speed of 25 K h^{-1} to 773 K, and then cooled to room temperature. The crystals $\text{Cs}_3\text{CaBi}(\text{P}_2\text{O}_7)_2$ were separated from the glass by washing with distilled water and air.

4.1.1.1.12. $\text{CaRb}_2\text{P}_2\text{O}_7$ and $\text{CaCs}_2\text{P}_2\text{O}_7$.

These two compounds were prepared by Lyutsko *et al.* [44] by heating a mixture of calcium dihydrogen diphosphate $\text{CaH}_2\text{P}_2\text{O}_7$ and M^1NO_3 ($\text{M}^1 = \text{Rb}, \text{Cs}$) at 1073 K, according to the following chemical reaction:



4.1.1.2. Crystallographic data.

The main crystallographic data are reviewed for the various diphosphates associated with calcium and classified from the hexagonal to the monoclinic system (Table 5).

Table 5. Main crystallographic data for the diphosphates associated with calcium, classified from the hexagonal to the triclinic system.

Compound	System	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
$\text{Ca}_5(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$	Hexagonal	$\text{D}_{6h}^3, \text{C}_{6v}^3$ or D_{3h}^2	2	11.88	11.88	9.83	[36]
$\text{Ca}_5\text{K}_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$		$\text{D}_{6h}^3, \text{C}_{6v}^3$ or D_{3h}^2	2	11.88	11.88	9.83	[36]
$\beta\text{-Ca}_2\text{P}_2\text{O}_7$	Tetragonal	P4_1	8	6.684	6.684	24.144	[41, 42]
$\text{Cs}_3\text{CaBi}(\text{P}_2\text{O}_7)_2$	Orthorhombic	$\text{P2}_1\text{2}_1\text{2}_1$	4	9.2873	9.4292	17.6162	[43]
CaCuP_2O_7	Monoclinic	$\text{P2}_1/\text{n}$	4	5.2104	8.0574 91.356	12.344	[35]
$\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$		$\text{P2}_1/\text{n}$	2	7.67	11.51 92.28	11.00	[36]
$\text{Ca}(\text{NH}_4)_2\text{H}_4(\text{P}_2\text{O}_7)_2$		$\text{C2}/\text{c}$	4	7.17	19.99 102.52	9.33	[36]
$\text{CaK}_2\text{H}_4(\text{P}_2\text{O}_7)_2$		$\text{C2}/\text{c}$	4	7.17	19.99 102.52	9.33	[36]
$\text{CaNH}_4\text{HP}_2\text{O}_7$		$\text{P2}_1/\text{n}$	8	10.523	17.672 90.47	7.266	[36, 37]
$\text{CaK}_2\text{P}_2\text{O}_7$		$\text{P2}_1/\text{n}$	4	9.79	5.69 104.03	12.97	[38]
$\text{CaNH}_4\text{NaP}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$		Cc	4	10.39	16.55 103.31	5.677	[39]
$\alpha\text{CaNa}_2\text{P}_2\text{O}_7 \cdot 4 \text{H}_2\text{O}$		Pc	2	5.689	8.586 106.3	10.565	[40]
$\beta\text{CaNa}_2\text{P}_2\text{O}_7 \cdot 4 \text{H}_2\text{O}$		Cc	4	10.380	16.980 104.4	5.750	[40]
$\text{CaRb}_2\text{P}_2\text{O}_7$		$\text{P2}_1/\text{n}$	4	10.012	5.784 104.79	13.070	[44]
$\text{CaCs}_2\text{P}_2\text{O}_7$		$\text{P2}_1/\text{n}$	4	10.302	5.946 104.73	13.182	[44]

4.1.1.3. Infrared characterization studies made on $\text{P}_2\text{O}_7^{4-}$ in $\beta\text{-Ca}_2\text{P}_2\text{O}_7$.

De Waal *et al.* [45] have studied the infrared spectrum of $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ at room temperature. The spectral stretching region between 1400 and 1000 cm^{-1} contains several peaks. The P-O-P symmetrical stretching modes were identified unambiguously at 725 cm^{-1} [45-50]. Because of the low intensity of modes in the bending region of the infrared spectra, the assignment is not clearly defined as in the case of stretching modes. The P-O-P asymmetrical stretching is identified at 972 cm^{-1} . In the interval

1211-1003 cm^{-1} , it was observed the PO_3 symmetrical and asymmetrical stretching modes (Table 6).

Table 6. Frequencies (cm^{-1}) of IR absorption bands for $\beta\text{-Ca}_2\text{P}_2\text{O}_7$.

Frequencies (ν/cm^{-1})	Assignment [45-50]
1211; 1188; 1172; 1157; 1138; 1102; 1086; 1078	$\nu_{\text{as}}(\text{PO}_3)$
1062; 1046; 1028; 1003	$\nu_{\text{s}}(\text{PO}_3)$
972; 943; 916	$\nu_{\text{as}}(\text{POP})$
791 ; 725	$\nu_{\text{s}}(\text{POP})$

4.2. Cyclophosphates.

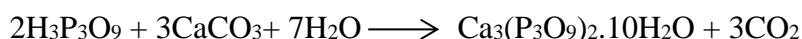
4.2.1. Cyclotriphosphates $\text{P}_3\text{O}_9^{3-}$.

4.2.1.1. Synthesis.

We present here the synthesis of the cyclotriphosphates associated with calcium by the various synthetic methods: ion-exchange resin and thermic method.

4.2.1.1.1. $\text{Ca}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$.

This compound was prepared by Belaaouad *et al.* [51] by adding dilute cyclotriphosphoric acid $\text{H}_3\text{P}_3\text{O}_9$ (0.67mol/l) slowly to an aqueous solution of calcium carbonate CaCO_3 (1mol/l), according to the following chemical reaction during 24 hours of mechanical stirring:



The obtained solution was then slowly evaporated at 25°C , until polycrystalline samples of $\text{Ca}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$ were obtained after 35 days. The $\text{H}_3\text{P}_3\text{O}_9$ used in this reaction was prepared from an aqueous solution of $\text{Na}_3\text{P}_3\text{O}_9$ passed through an ion-exchange resin.

4.2.1.1.2. $\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$.

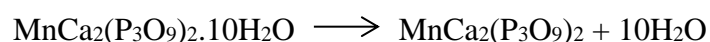
Tridane *et al.* [52,53], have prepared the titled compound by slowly adding diluted cyclotriphosphoric acid $\text{H}_3\text{P}_3\text{O}_9$ to an aqueous solution of calcium carbonate CaCO_3 and manganese carbonate MnCO_3 with a stoichiometric ratio $\text{Ca}/\text{Mn}=2$, according to the following chemical reaction:



The obtained solution was then slowly evaporated at room temperature until large rectangular prisms of $\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$ are obtained.

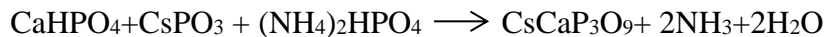
4.2.1.1.3. $\text{MnCa}_2(\text{P}_3\text{O}_9)_2$.

The anhydrous form has also been obtained by Tridane *et al.* [52,53] by total dehydration of $\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$ under atmospheric pressure between 400 and 450°C , as the following chemical reaction:



4.2.1.1.4. CsCaP₃O₉.

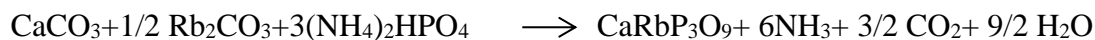
This compound was obtained by Zatovsky *et al.* [54] by the conventional solid-state method. Using diammonium hydrogen phosphate (NH₄)₂HPO₄, CsPO₃, and CaHPO₄ as starting materials. A mixture of 2.11 g of (NH₄)₂HPO₄, 5g of CsPO₃, and 0.952 g of CaHPO₄ was ground and then heated to 973 K for 3 h, according to the following chemical reaction:



The resulting melt was kept at this temperature for 30 min and finally cooled to room temperature. Crystals of CsCaP₃O₉ were separated from the rest of the glassy matrix by washing with hot deionized water.

4.2.1.1.5. CaRbP₃O₉.

This compound has been obtained by Henry *et al.* [32] from a mixture of calcium carbonate CaCO₃, rubidium carbonate RbCO₃, and diammonium hydrogen phosphate (NH₄)₂HPO₄ at 400°C for one week, according to the following chemical reaction:

4.2.1.1.6. CaNH₄P₃O₉.

This compound was prepared by Masse *et al.* [55,56], from a mixture of calcium carbonate CaCO₃, and diammonium hydrogen phosphate (NH₄)₂HPO₄ at 300°C, according to the following chemical reaction:

4.2.1.1.7. CaNH₄P₃O₉.3H₂O.

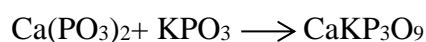
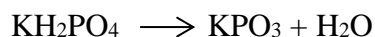
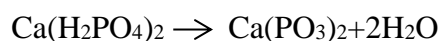
The salt was obtained by Masse *et al.* [55,56] by the Boullé method. Ag₃P₃O₉ was mixed with a solution of calcium chloride CaCl₂ and ammonium chloride NH₄Cl in stoichiometric proportions, according to the following chemical reaction:



The obtained solution was then slowly evaporated at room temperature; crystals of CaNH₄P₃O₉.3H₂O sufficiently strong and good qualities were obtained.

4.2.1.1.8. CaKP₃O₉.

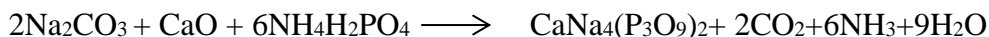
This compound has prepared by Sandström *et al.* [57] by mixing Ca(PO₃)₂ (obtained from dehydrated of Ca(H₂PO₄)₂ at 873 K) and KPO₃ (obtained from dehydrated of KH₂PO₄ at 873 K) in a 1:1 ratio, according to the following chemical reactions:



Crystals of CaKP_3O_9 were grown by heating a mixture consisting of 9 wt% KPO_3 and 91 wt% CaKP_3O_9 at 1173 K for about 12 h, followed by cooling at a rate of 6K h^{-1} to 997 K, and finally quenching to room temperature.

4.2.1.1.9. $\text{CaNa}_4(\text{P}_3\text{O}_9)_2$.

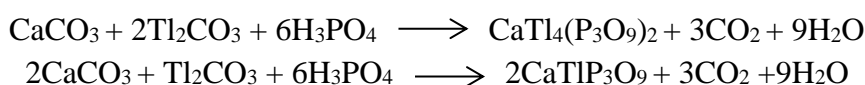
The title compound was prepared by Abrahams *et al.* [58,59] as a polycrystalline powder by crystallizing a glass of the stoichiometric composition. A mixture of sodium carbonate Na_2CO_3 , calcium oxide CaO and ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ were ground and heated hour at 1000 °C for 1 hour until molten, according to the following chemical reactions:



The melt was poured into hot graphite at 350 °C and allowed to cool slowly to room temperature in a furnace and was then reheated to 600 °C to facilitate crystallization. Single crystals of $\text{CaNa}_4(\text{P}_3\text{O}_9)_2$ were obtained by slow cooling of the melt in the furnace for 12 hours.

4.2.1.1.10. $\text{CaTl}_4(\text{P}_3\text{O}_9)_2$ and CaTlP_3O_9 .

By the conventional solid-state method, Rolaiso *et al.* [60] have prepared the two compounds using appropriate stoichiometric amounts of a large excess of phosphoric acid H_3PO_4 and calcium CaCO_3 , and thallium Tl_2CO_3 carbonates were mixed at around 400° C in an agate mortar, according to the following chemical reactions:



4.2.1.2. Crystallographic data.

The main crystallographic data obtained for the various cyclotriphosphates associated with calcium are classified from the hexagonal to the triclinic system, as illustrated in Table 7.

Table 7. Main crystallographic data for the cyclotriphosphate associated with calcium, classified from the hexagonal to the triclinic system.

Compound	System	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
$\text{MnCa}_2(\text{P}_3\text{O}_9)_2$	Hexagonal	P-31c	2	7.392	7.392	20.134	[52,53]
$\text{CaNH}_4\text{P}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$		P6 ₃	8	14.76	14.76	9.932	[55,56]
CaKP_3O_9		P-6c2	2	6.8090	6.8090	10.3760	[47]
$\text{CaTl}_4(\text{P}_3\text{O}_9)_2$		P3 ₁ c	2	7.389	7.389	19.99	[60]
$\text{CaNH}_4\text{P}_3\text{O}_9$		P-62c	2	6.887	6.887	10.448	[55,56]
CaCsP_3O_9	Orthorhombic	Pnma	4	9.8287	7.5642	12.7905	[54]
$\text{Ca}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$	Monoclinic	P2 ₁ /n	2	9.332	18.13 106.69	7.841	[51]
$\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$		P2 ₁ /n	2	9.631	18.173 109.44	7.976	[52,53]
CaRbP_3O_9		P2 ₁ /n	4	7.545	12.51	9.745	[32]
$\text{CaNa}_4(\text{P}_3\text{O}_9)_2$		C2/c	4	13.069	8.054 94.60	14.164	[58,59]
CaTlP_3O_9		P2 ₁ /n	4	7.471	12.52	9.913	[60]

4.2.1.3. Infrared characterization studies made on $\text{P}_3\text{O}_9^{3-}$ in $\text{Ca}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$.

Belaouad *et al.* [51] have studied the infrared spectrum of $\text{Ca}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$ at 25°C . In the range $4000\text{--}1600\text{ cm}^{-1}$, the IR spectrum showed four stretching bands at 3660 , 3580 , 1660 , and 1620 cm^{-1} . The bands at 3660 and 3580 cm^{-1} are attributed to the stretching vibrations of water molecules ($\nu\text{ O-H}$) [61-63]. The bands at 1660 and 1620 cm^{-1} represent the bending vibration of water molecules (δHOH) [61-63]. Between 1318 and 668 cm^{-1} , were observed the stretching modes $\nu_{\text{as}}\text{ OPO}$ and $\nu_{\text{s}}\text{OP}$ characteristic of phosphates with ring anions $\text{P}_3\text{O}_9^{3-}$ [64-66], as illustrated in Table 8.

The IR stretching vibrations of (POP) ring groups are observed as a very strong band at 1030 cm^{-1} for the $\nu_{\text{as}}\text{ POP}$ asymmetric vibrations and a strong band at 780 cm^{-1} for the $\nu_{\text{s}}\text{OP}$ symmetric vibrations. The vibration corresponding to the differences in observed bands is given in Table 8.

Table 8. Frequencies (cm^{-1}) of IR absorption bands for $\text{Ca}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$.

Infrared ($\nu\text{ /cm}^{-1}$)	Assignments [51]
3660; 3580	$\nu\text{O-H}$
1660; 1620	$\delta\text{ HOH}$
1318; 1272	$\nu_{\text{as}}\text{ OPO}$
1174; 1120	$\nu_{\text{s}}\text{ OPO}$
1030	$\nu_{\text{as}}\text{ POP}$
880; 780; 668	$\nu_{\text{s}}\text{ POP}$
562 ; 514	$\delta\text{ OPO}+\rho\text{ OPO}$

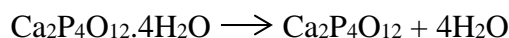
4.2.2. Cyclotetraphosphates $\text{P}_4\text{O}_{12}^{4-}$.

4.2.2.1. Synthesis.

The various synthetic methods of the cyclotetraphosphates associated with calcium are described for the following compounds:

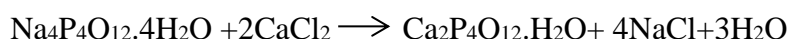
$\text{Ca}_2\text{P}_4\text{O}_{12}$

This compound was prepared by Shneider *et al.* [67] by thermal dehydration of the tetrahydrate $\text{Ca}_2\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$ under atmospheric pressure at 220°C , according to the following chemical reaction:



4.2.2.1.1. $\text{Ca}_2\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$.

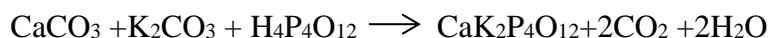
This salt was prepared by Skogareva *et al.* [68] by adding a solution of 4.495 g of $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$ in 50 ml water to a solution of 2.079 g of CaCl_2 in 10 ml of water, adopting the chemical reactions:



The resulting product was left to stand at room temperature for 2 hours for crystallization.

4.2.2.1.2. $\text{CaK}_2\text{P}_4\text{O}_{12}$.

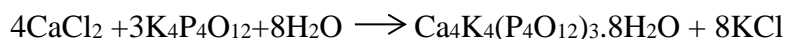
This salt was prepared by Cavero-Gherssi *et al.* [69] by attacking at 0°C, the stoichiometric mixture of calcium CaCO_3 and potassium K_2CO_3 carbonates with a titrated solution of tetrametaphosphoric acid $\text{H}_4\text{P}_4\text{O}_{12}$, according to the following chemical reaction:



The evaporation at an ambient temperature of the liquor thus obtained leaves $\text{CaK}_2\text{P}_4\text{O}_{12}$ salt to precipitate.

4.2.2.1.3. $\text{Ca}_4\text{K}_4(\text{P}_4\text{O}_{12})_3 \cdot 8\text{H}_2\text{O}$.

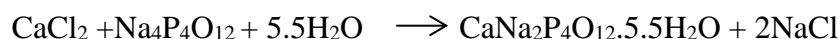
This compound was obtained by Averbuch-Pouchot [70] who has added very slowly to an aqueous solution of potassium cyclotetraphosphate one $\text{K}_4\text{P}_4\text{O}_{12}$ a concentrated aqueous solution of calcium chloride CaCl_2 , as illustrated by the chemical reaction:



After a few weeks, a crystalline crust was observed. The addition of calcium chloride is then stopped, and the system is kept at room temperature for a few more weeks. After filtration, well-developed crystals of $\text{Ca}_4\text{K}_4(\text{P}_4\text{O}_{12})_3 \cdot 8\text{H}_2\text{O}$ have been obtained.

4.2.2.1.4. $\text{CaNa}_2\text{P}_4\text{O}_{12} \cdot 5.5\text{H}_2\text{O}$.

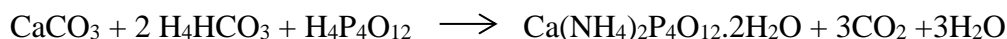
The same author [70] has prepared the $\text{CaNa}_2\text{P}_4\text{O}_{12} \cdot 5.5\text{H}_2\text{O}$ compound by slow evaporation at room temperature of an aqueous solution of sodium cyclo-tetraphosphate $\text{Na}_4\text{P}_4\text{O}_{12}$ and calcium chloride in stoichiometric ratio, according to the following $5\text{H}_2\text{O}$ chemical reaction:



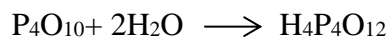
After filtration, well-developed crystals of $\text{CaNa}_2\text{P}_4\text{O}_{12} \cdot 5.2\text{H}_2\text{O}$ have been obtained.

4.2.2.1.5. $\text{Ca}(\text{NH}_4)_2\text{P}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$.

This crystal has been prepared by Tordjman *et al.* [71] by slow evaporation technique at 40 °C. To an aqueous solution of sodium cyclotetraphosphate $\text{Na}_4\text{P}_4\text{O}_{12}$, the authors have very slowly added an aqueous solution of calcium carbonate CaCO_3 and ammonium carbonate NH_4HCO_3 , according to the following chemical reaction:



After filtration, $\text{Ca}(\text{NH}_4)_2\text{P}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ crystals in the form of long needles were precipitated. The tetrametaphosphoric acid $\text{H}_4\text{P}_4\text{O}_{12}$ was prepared by the action of water maintained at 0°C on P_4O_{10} , according to the following chemical reaction:



4.2.2.2. Crystallographic data.

Herein, we report the main crystallographic data for the various cyclotetraphosphates associated with calcium classified from the hexagonal to the triclinic system (Table 9).

Table 9. Main crystallographic data for the cyclotetraphosphate associated with calcium, classified from the hexagonal to the triclinic system.

Compound	System	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
CaK ₂ P ₄ O ₁₂	Tetragonal	I-4	2	7.364	7.364	9.899	[69]
CaNa ₂ P ₄ O ₁₂ ·5.5H ₂ O	Orthorhombic	Pma2	4	27.88	7.536	7.378	[70]
Ca ₂ P ₄ O ₁₂ ·4H ₂ O	Monoclinic	P2 ₁ /n	4	7.668	12.895 107.00	7.144	[68]
Ca ₄ K ₄ (P ₄ O ₁₂) ₃ ·8H ₂ O		P2 ₁ /a	2	20.38	12.683 89.31	7.830	[70]
Ca(NH ₄) ₂ P ₄ O ₁₂ ·2H ₂ O		P2 ₁ /n	4	16.783	10.888 90.92	7.913	[71]
Ca ₂ P ₄ O ₁₂ ·H ₂ O	Triclinic	P1 or P-1	2	7.72 95.9	10.52 105.1	7.15 83.9	[68]
Ca ₂ P ₄ O ₁₂		P1 or P-1	2	8.02 97.4	10.42 109.8	7.20 90.4	[67]

For the anhydrous cyclotetraphosphate compounds, it is clearly stated that the substitution of 2K⁺ by Ca²⁺ induces the lowering symmetry from the tetragonal system in CaK₂P₄O₁₂ to the triclinic system in Ca₂P₄O₁₂.

4.2.2.3. Infrared characterization studies made on P₄O₁₂⁴⁻ in Ca₂P₄O₁₂·1.5H₂O·3H₂O.

Skogareva *et al.* [68] have studied the infrared spectrum of Ca₂P₄O₁₂·1.5H₂O·3H₂O at 25°C, which showed different characteristic regions of the anion P₄O₁₂⁴⁻:

- The spectral region 4000-3000 cm⁻¹, were observed the characteristic ν (O-H) stretching modes as a wide band around 3560- 3565 cm⁻¹ and a strong band at 3440 cm⁻¹.
- The range 1700-1600 cm⁻¹, where appeared a characteristic water deformation mode δ (H-O-H) of strong intensity at 1628 cm⁻¹.
- Between 1280 and 552 cm⁻¹, appeared the characteristic stretching modes of the P₄O₁₂⁴⁻ cycle [72,73]. Four strong bands observed at 1280, 1148, 1120, and 1020 cm⁻¹ were assigned to the antisymmetric stretching vibration ν_{as} (P-O), and the bands at 886, 800, and 740 cm⁻¹ to the symmetric stretching vibration ν_s (P-O). The symmetric vibration of the δ_s POP was assigned to the region of 676-440 cm⁻¹ (Table 10).

Table 10. Frequencies (cm⁻¹) of IR absorption bands for Ca₂P₄O₁₂·1.5H₂O·3H₂O.

Frequencies (cm ⁻¹)	Vibrations [68]
3440; 3560; 3656	ν (O-H)
1628	δ (H-O-H)
1280; 1148; 1120, 1020	ν_{as} (P-O)
886; 800; 740	ν_s (P-O)
676; 612; 552	ν_{as} OPO
496; 440; 400; 384; 352; 312	Ca-O(H ₂ O)

4.2.3. Cyclohexaphosphates $P_6O_{18}^{6-}$.

4.2.3.1. Synthesis.

In this part, we present the synthesis of the cyclohexaphosphates associated with calcium by various synthetic methods.

4.2.3.1.1. $Ca_2M_2P_6O_{18} \cdot 8H_2O$ (M: Li, Na).

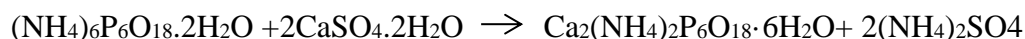
The two isotopic salts were prepared by Averbuch-Pouchot *et al.* [74] by adding solid gypsum $CaSO_4 \cdot 2H_2O$ to an aqueous solution of lithium and sodium cyclohexaphosphate $Li_6P_6O_{18} \cdot 6H_2O$, $Na_6P_6O_{18} \cdot 6H_2O$, according to the following chemical reaction:



After some days of evaporation at room temperature, crystals of $Ca_2Li_2P_6O_{18} \cdot 8H_2O$ and $Ca_2Na_2P_6O_{18} \cdot 8H_2O$ appeared as elongated prisms.

4.2.3.1.2. $Ca_2(NH_4)_2P_6O_{18} \cdot 6H_2O$.

This crystal was prepared by Averbuch-Pouchot *et al.* [75], by adding solid gypsum $CaSO_4 \cdot 2H_2O$ to an aqueous ammonium cyclohexaphosphate $(NH_4)_6P_6O_{18} \cdot 1H_2O$ at room temperature, according to the following chemical reaction:



After some days, the resulting product contains single crystals of $Ca_2(NH_4)_2P_6O_{18} \cdot 6H_2O$ sufficiently large and good quality.

4.2.3.1.3. $Ca_2Cs_2P_6O_{18} \cdot 2H_2O$.

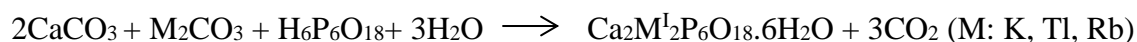
This crystal was prepared by Abid *et al.* [76] by adding dilute cyclohexaphosphoric acid $H_6P_6O_{18}$ to an aqueous solution of calcium carbonate $CaCO_3$ and cesium carbonate Cs_2CO_3 with a stoichiometric ratio $Ca/Cs = 1$, according to the following chemical reaction:



The obtained solution is then slowly evaporated at room temperature until large rectangular prisms of $Ca_2Cs_2P_6O_{18} \cdot 2H_2O$ was formed. The cyclohexaphosphoric acid $H_6P_6O_{18}$ was obtained from an aqueous solution of $Li_6P_6O_{18} \cdot 6H_2O$ passed through an ion-exchange resin.

4.2.3.1.4. $Ca_2M_2P_6O_{18} \cdot 6H_2O$ (M: K, Tl, Rb).

These three compounds were prepared by Abid *et al.* [77] by slowly adding dilute cyclohexaphosphoric acid $H_6P_6O_{18}$ to an aqueous solution of calcium carbonate $CaCO_3$ and M_2CO_3 [M = K, Tl, Rb] with a stoichiometric ratio $Ca/M = 1$ according to the flowing reaction:



After some days of slow evaporation at room temperature, crystals appeared with good quality.

4.2.3.2. Crystallographic data.

In this part, we reported the main crystallographic data for the various cyclohexaphosphate associated with calcium, classified from the hexagonal to the triclinic system (Table 11).

Table 11. Main crystallographic data for the cyclohexaphosphates associated with calcium, classified from the hexagonal to the triclinic.

Compound	System	Space group	Z	a(Å) α°	b(Å) β°	c(Å) γ°	References
Ca ₂ (NH ₄) ₂ P ₆ O ₁₈ ·6H ₂ O	Orthorhombic	P2 ₁ 2 ₁ 2	2	12.821	12.537	7.029	[75]
Ca ₂ CS ₂ P ₆ O ₁₈ ·2H ₂ O	Monoclinic	P2 ₁ /c	2	9.087	12.246 116.98	9.895	[76]
Ca ₂ K ₂ P ₆ O ₁₈ ·6H ₂ O		P2 ₁ /n	2	7.309	11.862 103.22	12.335	[77]
Ca ₂ Tl ₂ P ₆ O ₁₈ ·6H ₂ O		P2 ₁ /n	2	7.233	11.582 99.94	12.193	[77]
Ca ₂ Rb ₂ P ₆ O ₁₈ ·6H ₂ O		P2 ₁ /n	2	7.290	11.593 100.86	2.236	[77]
Ca ₂ Li ₂ P ₆ O ₁₈ ·8H ₂ O	Triclinic	P-1	1	7.767 105.17	10.144 102.76	7.225 84.95	[74]
Ca ₂ Na ₂ P ₆ O ₁₈ ·8H ₂ O		P-1	1	8.031 105.69	10.296 103.27	7.279 85.30	[74]

The calcium cyclohexaphosphates are all found to be hydrate compounds. It is to note that cyclohexaphosphate with ammonium cations (NH₄)₆P₆O₁₈·1H₂O crystallized in the orthorhombic system, being highly symmetrical rather than the symmetry of others compounds crystallized in monoclinic and triclinic systems.

4.2.3.3. Infrared characterization studies made on P₆O₁₈⁴⁻ in Ca₂K₂P₆O₁₈·6H₂O.

Abid *et al.* [76] have studied the infrared spectrum of calcium potassium cyclohexaphosphate hexahydrate, Ca₂K₂P₆O₁₈·6H₂O at 25°C (Table 12). The spectrum exhibits:

- Two broad bands at about 3600–3200 cm⁻¹ and another one at 1650 cm⁻¹ corresponding to the vibration of water molecules, ν (O-H).
- Various stretching vibration bands for which both positions, between 1300 and 600 cm⁻¹, and number are typical of a phosphoric ring anion [77-83]. In this type of anions, the O-P-O vibrations take place at relatively high frequencies, 1200 < ν_{as} < 1300 cm⁻¹ and 1050 < ν_s < 1200 cm⁻¹, and those corresponding to the P-O-P vibrations appear as a broadband ν_{as} around 960 cm⁻¹ and a doublet ν_s between 800 and 700 cm⁻¹.

Table 12. Frequencies (cm⁻¹) of IR absorption bands for Ca₂K₂P₆O₁₈·6H₂O.

Frequencies (cm ⁻¹)	Vibrations [76-83]
3600- 3200	ν (O-H)
1650	δ (H-O-H)
1200-1300	ν_{as} O-P-O
1200-1050	ν_s O-P-O
960	ν_{as} P-O-P
700-800	ν_s P-O-P

5. Conclusions

In this review article, we have presented the various chemical methods used to prepare monophosphates and condensed phosphates associated with calcium. Besides, we have reported and analyzed their crystallographic data. The monophosphates containing (PO₄)³⁻

groups crystallized in the hexagonal, rhombohedral, trigonal, orthorhombic, and monoclinic systems, while the compounds with $(\text{HPO}_4)^{2-}$ and $(\text{H}_2\text{PO}_4)^-$ have low symmetry systems (monoclinic and triclinic). The long polyphosphates chain $(\text{PO}_3^-)_n$, containing one $(\text{PO}_4)^{3-}$ grouper formula, crystallized in the high possible symmetry (tetragonal systems), against that of formula with two, three, and four $(\text{PO}_4)^{3-}$ groups, which crystallized in the lower symmetry systems (monoclinic, and triclinic). In the anhydrous cyclotetraphosphates, the substitution of 2K^+ by Ca^{2+} induced lowering symmetry from the tetragonal system in $\text{CaK}_2\text{P}_4\text{O}_{12}$ to the triclinic system in $\text{Ca}_2\text{P}_4\text{O}_{12}$. The calcium cyclohexaphosphates all hydrate crystallized in the orthorhombic system, as a highly symmetrical system, where the cations are ammonium $(\text{NH}_4)_6\text{P}_6\text{O}_{18} \cdot 1.5\text{H}_2\text{O}$. Finally, infrared spectroscopy of some characteristic anions PO_3^{3-} in $\gamma\text{-Ca}(\text{PO}_3)_2$, PO_4^{3-} in CaHPO_4 , $\text{P}_2\text{O}_7^{4-}$ in $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, $\text{P}_3\text{O}_9^{3-}$ in $\text{MnCa}_2(\text{P}_3\text{O}_9)_2$, $\text{P}_4\text{O}_{12}^{4-}$ in $\text{Ca}_2\text{P}_4\text{O}_{12} \cdot 1.5\text{H}_2\text{O} \cdot 3\text{H}_2\text{O}$, and $\text{P}_6\text{O}_{18}^{6-}$ in $\text{Ca}_2\text{K}_2\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ have been reviewed.

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Conflicts of Interest

The authors declare no conflict of interest.

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