

# Chemical preparations, crystal data for monophosphates and condensed Phosphates associated to manganese and IR studies of their anions

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## ABSTRACT

The monophosphates and condensed phosphates associated with manganese, which are the subject of this article are an important part of phosphate chemistry and have been the subject of numerous studies and applications in many areas of Materials research and industry. In order to collect the unit cell parameters of these compounds, to establish a database of formulas existing up to now and to get an idea of the ease and difficulty of their preparation, we are concentrating the current research on chemical preparations, crystal data and IR studies for condensed phosphates and monophosphates. This work presents the chemical preparations, the main crystallographic data for manganese associated condensed phosphates and monophosphates, and the characterization by infrared vibration spectrometry for anions  $\text{PO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{P}_3\text{O}_9^{3-}$ ,  $\text{P}_4\text{O}_{12}^{4-}$ ,  $\text{P}_6\text{O}_{18}^{6-}$  and  $\text{P}_{10}\text{O}_{30}^{10-}$  in different compounds.

**Keywords:** Engineering Techniques, Chemical preparation, chemical analyses, crystallographic characterization, infrared vibration spectrometry, monophosphates, condensed Phosphates manganese

## 1. INTRODUCTION

Manganese is a heavy metal, part of the transition elements. Silvery, hard and brittle, it has magnetic properties [1]. The metal is chemically reactive: it oxidizes in the air but it does not react with water under normal conditions [2]. Its electronegativity leads it to form ionic bonds with oxides, hydroxides and carbonates. It thus forms unstable complexes (oxides, silicates, carbonates), most of which are less soluble than its hydroxides [3]. Manganese has common properties with cobalt and iron and the similarities between their respective behaviors are numerous [4].

The choice of manganese study associated with condensed phosphates and mono phosphates is justified by the properties

physical-chemical that presents this element. Phosphate chemistry is a vast field of research in which a large number of laboratories around the world are engaged. Research work on these compounds, far from being exhausted, has on the contrary intensified particularly during the last thirty years. The main reasons for this intensification are Phosphate chemistry is a vast field of research in which a large number of laboratories around the world are engaged. Research work on these compounds, far from being exhausted, has on the contrary intensified particularly during the last thirty years. The main reasons for this intensification are the discovery and growth of new methods of synthesis of phosphate-based compounds, the development of new indexing and structural resolution programs related to structural characterization techniques. The search for materials likely to have particular interesting properties and which can therefore be used in the fields applied. The present work describes the chemical preparations and reports crystal data for condensed phosphates and monophosphates associated to manganese and IR vibration spectrometry studies of their anions.

## 2. ELABORATION AND CRYSTAL DATA

The basic element of the constitution of all the phosphoric anions is the entity that we will designate most often under the name of  $\text{PO}_4$  tetrahedron or  $\text{PO}_4$  group [5]. This entity is constituted by a central atom of phosphorus (P) surrounded by four oxygen atoms building around it an almost regular tetrahedron. A phosphoric anion consists of one, (case of monophosphates), or several of these entities pooling vertices (case of condensed phosphates).

We can first divide all the phosphates into two categories: monophosphates and condensed phosphates and give two strict definitions to differentiate them: monophosphate is a salt whose anion consists of an isolated  $\text{PO}_4$  group and condensed phosphate is a salt whose anionic entity formed of several  $\text{PO}_4$  tetrahedra sharing vertices, thus contains one or more P-O-P bonds.

### 3. INFRARED VIBRATION SPECTROMETRY

Spectra were recorded in the range 4000-400  $\text{cm}^{-1}$ , with a Perkin-Elmer IR 983G spectrophotometer, using samples dispersed in spectroscopically pure KBr pellets.

#### 3.1 Monophosphates $\text{PO}_4^{3-}$

On the first of these families whose anionic entity is simple, since formed of an isolated  $\text{PO}_4$  group, no comment is necessary. We can simply add that the compounds of this family, long known as orthophosphates, are now known under the name of monophosphates.

In this part we present the synthesis of monophosphate associated with manganese by the various synthetic methods: synthesis by solid state diffusion, synthesis hydrothermal or synthesis by soft chemistry, structural characterization thus studies by IR vibration spectrometry of their anions. We have been able to isolate and characterize several phosphates of  $\text{Mn-PO}_4$  type as an example:  $\text{MnHPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{RbMnPO}_4$ ,  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{NaMnPO}_4$ ,  $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ ,  $\text{Mn}_{0.5}\text{Co}_{0.5}\text{NH}_4\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Mn}_3(\text{PO}_4)_2$ ,  $\text{LiMnPO}_4$ ,  $\text{Li}_3\text{V}_{2-x}\text{Mn}_x(\text{PO}_4)_3$ ,  $\text{KMnPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CsMnPO}_4$ ,  $\text{RbMnPO}_4$ ,  $\text{Ca}_{1.54}\text{Mn}_{1.46}\text{Fe}(\text{PO}_4)_3$ .

#### 3.2 Sample preparation

##### 1. $\text{MnHPO}_4 \cdot \text{H}_2\text{O}$

The  $\text{MnHPO}_4 \cdot \text{H}_2\text{O}$  [6] compound was prepared by solution precipitation method using Mn (complexometric), 99.99 %, Merck) and phosphoric acid (86.4 %w/w  $\text{H}_3\text{PO}_4$  Merck) as starting materials. In typical procedure, about 0.5 g of Mn (c) was dissolved in 5 mL of 1 M  $\text{H}_3\text{PO}_4$ . The resulting solution was stirred until  $\text{H}_2(\text{g})$  was completely evolved and the green gray precipitates were obtained (about 10min). The prepared solid was filtered by suction pump, washed with water and dried in air.

##### 3.3 $\text{RbMnPO}_4$

A powder sample of  $\text{RbMnPO}_4$  [7] was prepared by direct solid state reaction from stoichiometric mixtures of  $\text{Rb}_2\text{CO}_3$ ,  $\text{MnO}$ , and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  powders as previously reported. The mixture was fired at 500 °C in argon atmosphere for 2 days, and then the mixture was ground, pelletized, and heated at 800 °C for 36 h and at 1050 °C for 24 h with intermediate grindings to ensure a total reaction. The resulting powder sample is very fine and light beige. Sample purity was checked by laboratory powder X-ray diffraction.

##### 3.4 $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$

$\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  [8] micro-nanostructures,  $\text{M}_1$ - $\text{M}_3$  and  $\text{M}_6$ : Manganous chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) and ammonium phosphate ( $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ ) were used as manganese cation and phosphate anion precursors, respectively. Typically, 3.0 g

of ammonium chloride and 0.2 g of ammonium phosphate was added to a beaker and then 40 mL ethylene glycol ( $\text{M}_1$ ) or 20 mL water and 20 mL ethylene glycol ( $\text{M}_2$ ), or 20 mL water and 20 mL glycerol ( $\text{M}_3$ ), or 20 mL water and 20 mL polyethylene glycol ( $\text{M}_6$ ) was added. Mixture was stirred at room temperature until solid were completely dissolved then 0.2g  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was added to mixed solution and vigorous magnetic stirring at room temperature for 12 h. The obtained homogeneous white precipitates were washed with deionized water and ethanol several times and dried.

$\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  micro-nanostructures,  $\text{M}_4$ - $\text{M}_5$ : 3.0g of ammonium phosphate was added to a beaker and then 80 mL ethylene glycol ( $\text{M}_4$ ) or 40 mL ethylene glycol ( $\text{M}_5$ ) was added. Mixture was stirred at room temperature until solid were completely dissolved. Then, 0.2 g  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was added to the mixed solution and vigorous magnetic stirring at room temperature for 12h. The subsequent synthesis procedure was the same as that described above.

##### 3.5 $\text{NaMnPO}_4 \cdot 3\text{H}_2\text{O}$

In a typical synthesis,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (20.00g),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (53.98g), and surfactant PEG (polyethylene glycol)-400 (2.0 mL) were put in a mortar, and the mixture was fully ground by hand with a rubbing mallet for 40 min. The grinding velocity was about 90 circles/ min, and the strength applied was moderate. The reactant mixture gradually became damp, and then a paste formed quickly. The reaction mixture was maintained at room temperature for 3 h. The mixture was washed with water to remove soluble inorganic salts until  $\text{SO}_4^{2-}$  ion could not be visually detected with 0.5  $\text{molL}^{-1}$   $\text{BaCl}_2$  solution. The solid was then washed with a small amount of anhydrous ethanol and dried at 70°C for 3h. The resulting material was subsequently determined to be the nanocrystalline  $\text{NaMnPO}_4 \cdot 3\text{H}_2\text{O}$  [9].

##### 3.6 $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$

The new phases  $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$  [10] were also obtained as a microcrystalline powder by solid-state reaction, employing as precursors  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{MnCO}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$ , in the same molar ratios used to obtain single crystals. The mixtures were heated at 300 °C in a porcelain crucible to decompose and remove the volatile species. Then accumulative treatments for 24 h each at 400, 500, 600, and 700°C for manganese samples to 800°C in the case of the nickel sample were performed.

##### 3.7 $\text{CsMnPO}_4$

The sample of phosphate  $\text{CsMnPO}_4$  was synthesized by the co-precipitation method, using the procedure earlier applied for  $\text{CsMgPO}_4$  synthesis and described in [11]. The starting reagents for synthesis were  $\text{CsCl}$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ . The provenance and purity of the reagents used in this study are listed in table 1. The purity of the starting

$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  is explained by the uncertainty in the  $\text{H}_2\text{O}$  content in this chemical. That is why the manganese concentration in the solution taken for synthesis was confirmed gravimetrically.

### 3.8 $\text{Mn}_3(\text{PO}_4)_2$

A novel phase transparent light-yellow crystals of distorted octahedral shape with a maximum size of about 0.5 mm was grown under hydrothermal conditions. A mixture of  $\text{Mn}_2\text{O}_3(\text{NH}_4)_3\text{PO}_4$  and  $\text{GaPO}_4$  in a weight ratio of 3:3:1 was placed in a titanium vessel with water and enclosed in a stainless steel bomb. A small amount of  $\text{B}_2\text{O}_3$  (7%) was added to the starting material as a mineralize that allowed keeping the pH of the solution close to a neutral value. The reaction time at  $T = 270^\circ\text{C}$  and  $P = 10\text{ MPa}$  was 20 days. Three phases formed under these Conditions, differing in crystal shapes and colors. Semi quantitative X-ray spectral analysis (Cam Scan 4DV+ EDA Link AN 1000) of the phase reported here showed the presence of Mn and P in the crystals in an atomic ratio of 3: 2. Its amount can be estimated to 45% of the total yield. The two other phases were semitransparent yellow flat needles of  $(\text{NH}_4)\text{Mn}_2\text{O}(\text{PO}_4)$  ( $\text{HPO}_4$ )( $\text{H}_2\text{O}$ ) (45%) and transparent crystals of turquoise color and irregular shape of  $\text{NH}_4\text{Ga}_2\text{Mn}(\text{PO}_4)_3(\text{H}_2\text{O})$  (10%) [12].

### 3.9 $\text{LiMnPO}_4$

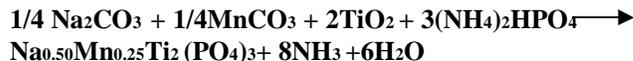
$\text{LiMnPO}_4$  [13] was synthesized in the following steps.  $\text{MnCl}_2$  (0.375 mol),  $\text{H}_3\text{PO}_4$  (0.375 mol) and ascorbic acid (12.5 g) were mixed and stirred. An aqueous solution containing  $\text{LiOH}$  (26.5 g) was slowly added into the mixed solution with stirring. The solution was further stirred for 2 hours and was then transferred into a high-pressure reactor placed in an oven at  $180^\circ\text{C}$  for 18 hours. The resulting precipitate was collected by centrifugal filtration and washed several times with deionized water before being dried at  $60^\circ\text{C}$  for 24 hours.  $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$  ( $x=0.2, 0.3, 0.4$ ) was prepared by the same procedure as  $\text{LiMnPO}_4$ .  $\text{MnCl}_2$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  totaled 0.375 mol with a varied Fe/Mn ratio. The  $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$  ( $x=0, 0.2, 0.3, 0.4$ )/C composite material was synthesized by mixing  $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$  ( $x=0, 0.2, 0.3, 0.4$ ) with glucose at a mass ratio of 4:1. The mixture was ball-milled for 6 hours, transferred into a tube furnace and sintered at  $700^\circ\text{C}$  for 5 hours under an Ar atmosphere.

### 3.10 $\text{KMnPO}_4$

$\text{KMnPO}_4 \cdot \text{H}_2\text{O}$  [14] was prepared by precipitation from aqueous solution by addition of a solution of  $\text{MnSO}_4$  to a large excess of concentrated  $\text{K}_2\text{HPO}_4$ . Powder neutron-diffraction data were obtained at 300 K and 1.7 K using the powder diffractometer D2B at the Institute Laue Langevin, Grenoble, France: The wavelength used was 1.594 Å. The crystal and magnetic structures were refined using the Rietveld method. The magnetization measurements were carried out in a magnetic field up to 6.5 T using an extraction method.

### 3.11 $\text{Na}_{0.50}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$

The compounds  $\text{Na}_{0.5}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$  ( $M = \text{Mn}, \text{Ni}$ ) are synthesized by a solid reaction method.



In the preparation, the titanium oxide " $\text{TiO}_2$ ", carbonates " $\text{M}^{\text{II}}\text{CO}_3$ ", and ammonium hydrogen phosphate " $(\text{NH}_4)_2\text{HPO}_4$ " were used as precursors. These reagents are milled for one hour in a porcelain mortar in order to achieve good homogenization and the finest particle size possible. The mixture is placed in a crucible and undergoes several heat treatments, at increasing temperatures, between each grinding operation, to ensure their homogeneity and promote solid state diffusion. They are finally brought to a temperature of  $1050^\circ\text{C}$  for 5 hours. The  $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$  ( $M = \text{Mn}, \text{Ni}$ ) powders are yellow and red [15].

## 4. SAMPLE CHARACTERIZATION

### 1. X-ray powder diffraction

The calculation of the unit-cell parameters and the analysis of the X-ray diffractogram enabled us to verify the purity of the synthesized product. The mesh parameters of these monophosphates are collected in table 1

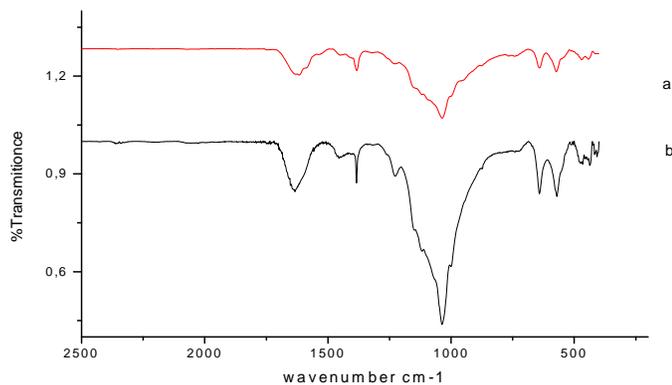
**Table 1:** Main crystallographic data for the monophosphates associated with manganese

Formula	a(Å) $\alpha(^{\circ})$	b(Å) $\beta(^{\circ})$	c(Å) $\gamma(^{\circ})$	S.G.	Z	References
$\text{MnHPO}_4 \cdot \text{H}_2\text{O}$	10.44	10.87	10.22	Pbca	8	[6]
$\text{RbMnPO}_4$	8.94635	5.43415 90.2912	9.10250	$P2_1$	Z	[7]
$\text{NaMnPO}_4 \cdot 3\text{H}_2\text{O}$	10.5280	6.3208	4.9851	$\text{Pmn}2_1$	Z	[9]
$\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$	17.991	6.648	10.765	$\text{Pn}2_1\text{a}$	Z	[10]
$\text{Mn}_3(\text{PO}_4)_2$	5.2344	6.6739 95.276	8.9688	$P2_1/n$	2	[12]
$\text{CsMnPO}_4$	91.185	5.839	5.65	$\text{Pna}2_1$	Z	[11]
$\text{LiMnPO}_4$	10.45139	6.10128	4.73492	$\text{Pmn}2_1$	Z	[13]
$\text{KMnPO}_4$	5.4813	8.6274	8.8865	$P4_1$	Z	[14]
$\text{Na}_{0.50}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$	14.60	13.31	2.67	Pmmm	4	[15]

### 2. Characterization of $\text{PO}_4^{3-}$ in $\text{Na}_{0.50}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ by IR vibration spectrometry.

The infrared absorption spectrum allowed us to characterize the compound and to verify the nature of the inserted species.

The characteristic absorptions of the compound are shown in Figure 1 [10].



**Figure 1:** Infrared spectra of: a)  $\text{Na}_{0.5}\text{Mn}_{0.25}\text{Ti}_2(\text{PO}_4)_3$ , b)  $\text{Na}_{0.5}\text{Ni}_{0.25}\text{Ti}_2(\text{PO}_4)_3$

The assignment of characteristic bands observed in the compound's spectra (Table) is made based on factor group analysis, and on previous results made on homologous compounds. Infrared spectroscopy analysis reveals several bands, in particular those attributable to  $\text{PO}_4^{3-}$  ions. The results are shown in Table 2.

**Table 2:** IR data for  $\text{Na}_{0.5}\text{M}_{0.25}\text{Ti}_2(\text{PO}_4)_3$  ( $\text{M} = \text{Mn}, \text{Ni}$ ), band positions and assignments

Frequencies $\nu(\text{cm}^{-1})$	Vibrations
500	$\delta_s \text{OPO}^-$ ( $\nu_2$ : symmetric deformation)
669	$\delta_{as} \text{OPO}^-$ ( $\nu_4$ : asymmetric deformation)
1316	$\nu_s \text{PO}$ ( $\nu_1$ : symmetric stretching)
1410	$\nu_{as} \text{PO}$ ( $\nu_3$ : asymmetric stretching)

This spectrum has four distinct frequency domains:

Domain I: between 1460 and 980  $\text{cm}^{-1}$  due to the anti-symmetric and symmetrical vibration of the  $\text{PO}_4^{3-}$  ion.

Domain II: between 660 and 500  $\text{cm}^{-1}$  corresponds to the anti-symmetric vibrations of deformation of the  $\text{PO}_4^{3-}$  ion

Domain III: between 450 and 400  $\text{cm}^{-1}$  due to the symmetrical vibration of the  $\text{PO}_4^{3-}$  ion.

Domain IV: less than 400  $\text{cm}^{-1}$  corresponds to external vibrations.

Based on the frequencies of the internal modes of the  $\text{PO}_4^{3-}$  ion, in the first frequency domain, we assign the frequency lines 1131, 1074, 1020 and 1001  $\text{cm}^{-1}$  to the anti-symmetric vibrations of the ion  $\text{PO}_4^{3-}$ .

The 982  $\text{cm}^{-1}$  frequency line is due to the symmetric valence vibrations relative to the  $\text{PO}_4^{3-}$  ion. The frequency bands 650, 621 and 550  $\text{cm}^{-1}$  correspond to the vibrations of anti-symmetric deformation of the  $\text{PO}_4^{3-}$  ion. Similarly, the

frequency lines 439, 401 and 349  $\text{cm}^{-1}$  are due to symmetrical deformation vibrations of the two  $\text{PO}_4^{3-}$  ions. The lines of frequency lower than 401  $\text{cm}^{-1}$  are due to the external vibrations of  $\text{PO}_4^{3-}$  ions, TiO groups.

## 5. CONDENSED PHOSPHATES

The complexity of classification appears with condensed phosphates because of the existence of several types of condensation geometries. We said that condensed phosphoric anions were constructed by a variable number of  $\text{PO}_4$  tetrahedra pooling vertices. A tetrahedron engaged in such a group may share one, two or three of its vertices with the adjacent tetrahedra. We will therefore have to distinguish three very different types of  $\text{PO}_4$  tetrahedra:

- Those whose only oxygen atom is engaged in a P-O-P bond which will be designated as terminal tetrahedra,
- Those who share two of their oxygen atoms with neighbouring tetrahedra which will be referred to as internal tetrahedra
- Those which share three of them and which are usually known neighbouring the names of ternary tetrahedra or branching tetrahedron.

### 5.1 Oligophosphates

We have seen above that in these salts the anionic groups are expressed by the general Formula  $[\text{P}_n\text{O}_{3n+1}]^-$ .

The valence of such a group being equal to  $(n+2)$ . Such anionic groups are currently known for  $n = 2, 3, 4$  and 5. Terminology used for this salt family has changed somewhat over time. Formerly known as pyrophosphates ( $n = 2$ ), tripolyphosphates ( $n = 3$ ) etc ... they now receive the shorter names of diphosphates ( $n = 2$ ), triphosphates ( $n = 3$ ) etc ... We summarize these two terminologies in Table 3.

**Table 3:** Nomenclature used for oligophosphates

N	Anions	Old nomenclature	Current nomenclature
2	$[\text{P}_2\text{O}_7]^{4-}$	Pyrophosphates	Diphosphates
3	$[\text{P}_3\text{O}_{10}]^{5-}$	Tripolyphosphates	Triphosphates
4	$[\text{P}_4\text{O}_{13}]^{6-}$	Tetrapolyphosphate	Tetraphosphates (linear) Isotetraphosphates (amified)
5	$[\text{P}_5\text{O}_{16}]^{7-}$	Pentapolyphosphates	Pentaphosphates

#### 1. $\text{P}_2\text{O}_7^{4-}$

In this part we present the synthesis of Diphosphates associated with manganese by the various synthetic methods, structural characterization thus studies by IR vibration spectrometry of their anions. We have been able to isolate and

characterize several phosphates of Mn-P<sub>2</sub>O<sub>7</sub> type as an example:

ZnMnP<sub>2</sub>O<sub>7</sub>, Sr<sub>2</sub>Mn[PO<sub>4</sub>][P<sub>2</sub>O<sub>7</sub>], Na<sub>4</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>), Ni<sub>1,184</sub>Mn<sub>0,816</sub>P<sub>2</sub>O<sub>7</sub>, MnNiP<sub>2</sub>O<sub>7</sub> and LiMn(H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

### 5.1.1 Sample preparation

#### 1. ZnMnP<sub>2</sub>O<sub>7</sub>

ZnMnP<sub>2</sub>O<sub>7</sub> diphosphate is prepared in powder by the ceramic method from the reagents ZnCO<sub>3</sub>, MnCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, these reagents taken in stoichiometric proportions are finely ground in an agate mortar. Afterwards, the mixture is placed in a silica crucible, kept in air at 120 °C for 15 hours and gradually brought to 500 °C in order to avoid a sudden decomposition of carbonates or ammonium hydrogenophosphate. Once the decomposition is complete, the mixture is well-grounded and treated at 900 °C for 24 hours. Finally, the powder is quenched in the air [16].

#### 2. Sr<sub>2</sub>Mn[PO<sub>4</sub>][P<sub>2</sub>O<sub>7</sub>]

(59 mg, 0.4 mmol), Mn<sub>2</sub>O<sub>3</sub> (63 mg, 0.4 mmol) and 0.2 ml of 85 % H<sub>3</sub>PO<sub>4</sub>. A reaction mixture was loaded into quartz tubes and filled with 0.5 ml water. The autoclave was heated at 375 °C for 3 days and then cooled to room temperature. The solid products were recovered by suction filtration and washed with distilled water. Very few red block-like crystals of the title compound were obtained. However, the reproduction of the crystal preparation was not successful [17].

#### 3. Na<sub>4</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)

Na<sub>4</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>) was synthesized via a conventional solid-state reaction. A stoichiometric quantity of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (95 %, Aldrich), Mn<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (99%, Alfa Aesar) and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (98% ACS reagent, Aldrich) was mixed using wet ball milling at 200 rpm for 12 hours in acetone. Following ball-milling, the acetone was dried out at 70°C for 12 hours. The mixture was calcinated at 300°C for 6 hours in air, and the resulting powder was pelletized under a pressure of 200 kg cm<sup>-2</sup>, and sintered again at 600°C for 6 hours in air. Carbon coating of the Na<sub>4</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>) sample was carried out to enhance the electrical conductivity using pyromellitic acid (PA) (C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>, 96%, Alfa Aesar). Na<sub>4</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>), and PA were mixed using a planetary ball-milling with a mass ratio of 9:1, and the ground mixture was annealed at 600°C for 2 hours under an Ar atmosphere. The carbon content was approximately 3 wt% of the total powder sample [18].

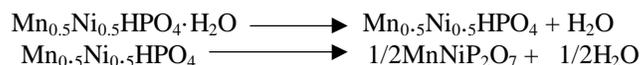
#### 4. Ni<sub>1,184</sub>Mn<sub>0,816</sub>P<sub>2</sub>O<sub>7</sub>

All samples were prepared by direct fusion. Stoichiometric quantities of NiO, MnCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> were ground together and heated in a platinum crucible to 393 K for 15 h and then progressively to 773 K and then 923 K. After the evolution of CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O from the decomposition of the carbonate and ammonium hydrogen phosphate ceased, the

temperature of the mixture (after regrinding) was raised to 1173 K for 20 h. The material was cooled in air to room temperature [19].

### 5. MnNiP<sub>2</sub>O<sub>7</sub>

The binary Mn<sub>0.5</sub>Ni<sub>0.5</sub>HPO<sub>4</sub>·H<sub>2</sub>O compound was prepared by the solution coprecipitation method using Mn(c) (c, complexometric) (99.99%, Merck), NiCO<sub>3</sub> (99.99%, Merck), and H<sub>3</sub>PO<sub>4</sub> (86.4% w/w, Merck) as starting materials. Following the procedure, 1.3894 g of Mn(c) and 1.4293 g of NiCO<sub>3</sub> (a mole ratio corresponding to the nominal composition of Mn: Co ratio of 1.0:1.0) were dissolved in 70% H<sub>3</sub>PO<sub>4</sub> (86.4% w/w H<sub>3</sub>PO<sub>4</sub> dissolved in deionized (DI) water) with continuous stirring at ambient temperature. The resulting solution was stirred until CO<sub>2</sub>(g) was completely evolved (5-15 min) and the precipitate was obtained. Then 10 mL of acetone was added to the obtained nearly dry sample to allow a highly crystalline products to be developed. The pale green solid of Mn<sub>0.5</sub>Ni<sub>0.5</sub>HPO<sub>4</sub>·H<sub>2</sub>O product was filtered by a suction pump, washed with acetone until free from phosphate ion, and dried in air. Its final decomposition product seemed to occur at temperatures above 673 K (Figure 1). The dried pale green solid than was calcined in a box furnace at 773 K for 2 h in air. The final product was obtained as a pale blue solid [20].



### 6. LiMn(H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>

The title compound was synthesized from a mixture of Mn<sub>2</sub>O<sub>3</sub> (1.5 g) and concentrated H<sub>3</sub>PO<sub>4</sub> (30 mL, 85%) placed in a borosilicate beaker and stirred at 250 °C until completely dissolved. Afterward, Li<sub>2</sub>CO<sub>3</sub> (5 g) was added, corresponding to the molar ratio Li: Mn: P of 13.5:1.9:42. The mixture was stirred for 24 h. The resulting purple precipitate was washed with water, filtered, and finally washed with acetone [21].

### 7. BaMnP<sub>2</sub>O<sub>7</sub> monoclinic

A mixture of BaCO<sub>3</sub> (0.987 g, 5.00 mmol), MnO<sub>2</sub> (0.435 g, 5.00 mmol) and P<sub>2</sub>O<sub>5</sub> (0.710 g, 5.00 mmol) was ground thoroughly in a mortar, and then transferred to a ceramic crucible. The crucible was then placed in the tube furnace and heated in air to 1100°C for 72 h. At the end of the heating period, the furnace was cooled slowly (approximately 5°C/min) to room temperature. At this temperature the sample was removed from the oven. A yellow crystal was cleaved from the bulk sample and analysed by single-crystal diffraction. It was found to belong to the monoclinic crystalline system [22].

### 8. BaMnP<sub>2</sub>O<sub>7</sub> triclinic

A mixture of BaCO<sub>3</sub> (0.987 g, 5.00 mmol), MnO<sub>2</sub> (0.436 g, 5.01 mmol) and P<sub>2</sub>O<sub>5</sub> (0.710 g, 5.00 mmol) was ground thoroughly in a mortar, and then transferred to a ceramic

crucible. The crucible was then placed in the oven (Thermolyne Model F21125) and heated in air to 1000°C for 72 h. After the heating period, the oven was cooled slowly (approximately 5°C/min) to room temperature.

At this temperature the sample was removed from the oven. A yellow crystal was cleaved from the bulk sample and analysed by single crystal diffraction. It was found to belong to the triclinic crystalline system. An X-ray powder diffraction analysis indicated the bulk sample to be the pure triclinic form [22].

## 5.1.2 Sample characterization

### 1. X-ray powder diffraction

The calculation of the mesh parameters and the analysis of the X-ray diffractogram enabled us to verify the purity of the synthesized product. The mesh parameters of these monophosphates are collected in table 4

**Table 4:** Main Crystallographic data for the

Formula	a(Å) α(°)	b(Å) β(°)	c(Å) γ(°)	S.G.	Z	References
ZnMnP <sub>2</sub> O <sub>7</sub>	6.6141	8.4366	4.5305	C2/m	2	[16]
Sr <sub>2</sub> Mn [PO <sub>4</sub> ][P <sub>2</sub> O <sub>7</sub> ]	6.641	6.8341 103.948	9.554	P12 <sub>1</sub> /c 1	4	[17]
Na <sub>4</sub> Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (P <sub>2</sub> O <sub>7</sub> ) )	17.991	6.648	10.765	Pna2 <sub>1</sub>	4	[18]
Ni <sub>1.184</sub> Mn <sub>0.816</sub> P <sub>2</sub> O <sub>7</sub>	6.557	8.738 103.240	4.498	Cm	2	[19]
MnNiP <sub>2</sub> O <sub>7</sub>	6.546	8.438 102.88	4.616	C2/m	4	[20]
LiMn(H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	11.1359	12.8206 105.73	8.6934	C12/C1	4	[21]
BaMnP <sub>2</sub> O <sub>7</sub>	12.825	8.633 90.08	5.5537	P2 <sub>1</sub> /n	2	[22]
BaMnP <sub>2</sub> O <sub>7</sub>	5.473 102.10	7.59 86.03	7.166 89.29	P-1	2	[22]

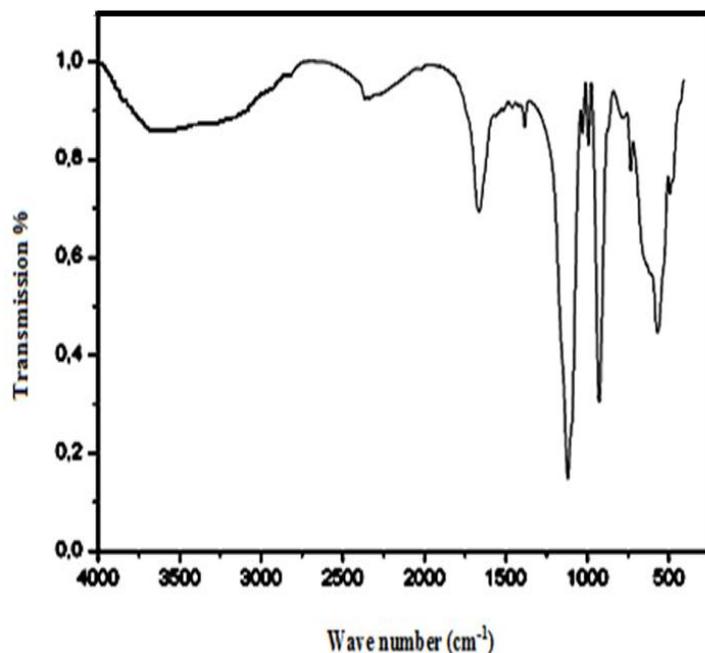
diphosphates associated to manganese

### 2. Characterization of P<sub>2</sub>O<sub>7</sub><sup>4-</sup> in BaMnP<sub>2</sub>O<sub>7</sub> by IR vibration spectrometry.

IR absorption spectra of various compounds are recorded in the interval 1500-350 cm<sup>-1</sup>, absorption field of the ions contained in condensed phosphates. As for the Raman scattering spectra, they are derived from 25 to 1500 cm<sup>-1</sup>, including the field of external modes of cations and anions. Table 5 contains the main stretching and bending vibrations of P<sub>2</sub>O<sub>7</sub><sup>4-</sup> anions [23].

**Table 5:** IR Frequency characteristics (in cm<sup>-1</sup>) for P<sub>2</sub>O<sub>7</sub><sup>4-</sup> anions

Frequencies ν(cm <sup>-1</sup> )	Vibrations
1115 – 1250 cm <sup>-1</sup>	ν <sub>as</sub> (PO <sub>3</sub> )
1110 – 990 cm <sup>-1</sup>	ν <sub>s</sub> (PO <sub>3</sub> )
960- 720 cm <sup>-1</sup>	ν <sub>as</sub> (POP)
660- 529 cm <sup>-1</sup>	δ <sub>as</sub> (PO <sub>3</sub> )
529- 300 cm <sup>-1</sup>	δ <sub>s</sub> (PO <sub>3</sub> )



**Figure 2:** IR spectrum of the phosphate BaMnP<sub>2</sub>O<sub>7</sub>

In this part we present the synthesis of Diphosphates associated with manganese by the various synthetic methods, structural characterization thus studies by IR vibration spectrometry of their anions. We have been able to isolate and characterize several phosphates of Mn-P<sub>2</sub>O<sub>7</sub> type as an example.

### Mn<sub>0.5</sub>NH<sub>4</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O

Solutions of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O (0.1M), NH<sub>4</sub>Cl (0.1 M) and MnCl<sub>2</sub>·4H<sub>2</sub>O (0.1 M) were mixed with a few mL of concentrated HCl. The resulting solution was left at 30°C in bath of sand, and after 4 days pink crystals of Mn<sub>0.5</sub>NH<sub>4</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O appeared. Mn<sub>0.5</sub>NH<sub>4</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>·H<sub>2</sub>O [24] diphosphate crystallizes in the triclinic system, space group P-1 (C<sub>1</sub>), with two molecules per cell with the following

unit-cell dimensions : $a=7.0029(2)\text{\AA}$ ,  $b = 7.4401(2)\text{\AA}$ ,  $c = 7.8771(2)\text{\AA}$ ,  $\alpha = 80.444(1)^\circ$ ,  $\beta = 71.359(1)^\circ$ ,  $\gamma = 87.408(1)^\circ$ ,  $V = 383.48(2)\text{\AA}^3$ .

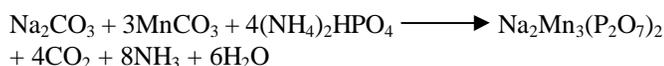
## 2. $P_3O_{10}^{4-}$

In this part we present the synthesis of Triphosphates associated with manganese by the various synthetic methods, structural characterization thus studies by IR vibration spectrometry of their anions. We have been able to isolate and characterize several phosphates of  $Mn-P_3O_{10}$  type as an example.

### 5.1.3 Sample preparation

#### 1. $NaMn_6(P_2O_7)_2(P_3O_{10})$

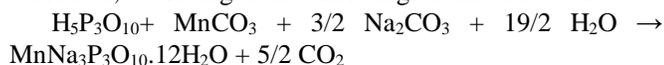
The starting materials  $Na_2CO_3$  [for (I)] or  $KNO_3$  [for (II)],  $MnCO_3$  (or  $CdCO_3$ ) and  $(NH_4)_2HPO_4$  were mixed in a stoichiometry expected to lead to the preparation of  $A_2B_3(P_2O_7)_2$ , with  $A=Na$  and  $B=Mn$  for (I), and  $A=K$  and  $B=Cd$  for (II), according to the following two reactions:



The starting mixture was heated slowly to 873 K to eliminate  $NH_3$ ,  $CO_2$  [and  $NO_2$  in (II)] and  $H_2O$ , followed by heating to 1223 K [for (I)] or 1023 K [for (II)] and slow cooling (6 Kh $\ddot{y}$ l) to 673 K, whereupon the furnace was allowed to cool to ambient temperature without control. Colorless crystalline solids were obtained [25].

#### 2. $MnNa_3P_3O_{10} \cdot 12H_2O$

Polycrystalline samples of the  $MnNa_3P_3O_{10} \cdot 12H_2O$ , were prepared by adding slowly dilute triphosphoric acid to an aqueous solution of nickel II carbonate and sodium carbonate, according to the following chemical reaction:



The preliminary obtained solution was then slowly evaporated at room temperature until Polycrystalline samples of  $MnNa_3P_3O_{10} \cdot 12H_2O$  were obtained. The triphosphoric acid used in this reaction was prepared from an aqueous solution of  $Na_5P_3O_{10}$  passed through an ion-exchange resin "Amberlite IR 120". The solution passage rate through the cation exchanger was 2mL/min [26].

### 5.1.4 Sample characterization

#### 1. X-ray powder diffraction

The calculation of the mesh parameters and the analysis of the X-ray diffractogram enabled us to verify the purity of the synthesized product. The mesh parameters of these Triphosphates are collected in table 6.

**Table 6: Main Crystallographic Data for the Triphosphates associated to manganese.**

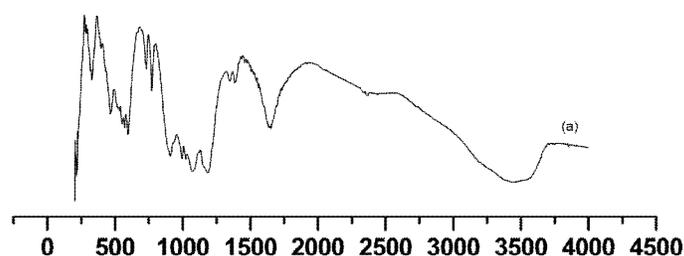
Formula	a( $\text{\AA}$ ) $\alpha$ ( $^\circ$ )	b( $\text{\AA}$ ) $\beta$ ( $^\circ$ )	c( $\text{\AA}$ ) $\gamma$ ( $^\circ$ )	S.G.	Z	References
$NaMn_6(P_2O_7)_2(P_3O_{10})$	5.3452	6.620 107.28	6.559	$P2_1/m$	2	[25]
$MnNa_3P_3O_{10} \cdot 12H_2O$	14.71	9.33 89.8	15.13	$P2_1/n$	4	[26]

### S.G. Space Group

## 2. Characterization of $P_3O_{10}$ in $MnNa_3P_3O_{10} \cdot 12H_2O$ by IR vibration spectrometry.

The infrared (IR) spectrum (Fig. 3) for kanonerovite was obtained by a Perkin Elmer Fourier spectrometer on a KBr pellet containing about 0.001 mg of kanonerovite. The positions ( $cm^{-1}$ ) of the main absorption bands are as follows: 447, 519, 558, 668, 875, 908, 992, 1034, 1117, 1153, 1327, 1590, 1650, 3311, 3394, and 3586

The band corresponding to the P–O asymmetrical stretching vibrations has its maximum at  $1117\text{ cm}^{-1}$  and indicates condensation of P-tetrahedra (Mel'nikova et al. 1985); for orthophosphates this maximum is usually localised in the  $1020 - 1080\text{ cm}^{-1}$  range. The large splitting of the band corresponding to the bending O–P–O-vibrations (558– 668  $cm^{-1}$ ) is also characteristic for condensed (but not orthophosphates). Furthermore, the  $908\text{ cm}^{-1}$  band of symmetric stretching vibrations of  $PO_4$ -tetrahedra is characteristic for the condensed phosphates, while in orthophosphates this band is shifted towards higher frequencies ( $940 - 960\text{ cm}^{-1}$ ) [26].



**Figure 3: IR spectrum of the phosphate  $MnNa_3P_3O_{10} \cdot 12H_2O$**

**Table 7: Characterization of  $MnNa_3P_3O_{10} \cdot 12H_2O$  by IR vibration spectrometry**

Frequencies $\nu(cm^{-1})$	Vibrations
3470	$\nu O-H$
1653	$\nu_8 HOH$
1360	$\nu P=O$
1253	$\nu_{as} PO_2$

1214	$v_{as}PO_2$
1188	$v_{as}PO_3$
1102	$v_s PO_2$
973	$v_s PO_3$
925	$v_{as}POP$
813	$v_{as}POP$
773	$v_s POP$
756	$v_s POP$
683	$v_s POP$
605	$\delta PO_2$
562	$\delta PO_3$

### 3. $P_4O_{13}^{6-}$ , $P_5O_{16}^{7-}$

Till now, there are no oligophosphates associated to manganese for such anions  $P_4O_{13}$

### 5.2 Cyclophosphates ( $P_nO_{3n}$ )<sup>n-</sup>

The second type of condensation observed for anions for which the O/P ratio is equal to three ducts to finite cyclic entities generally formulated:  $[P_nO_{3n}]^{n-}$ . In such an anionic arrangement each tetrahedron shares two of its oxygen atoms with adjacent tetrahedrons. The local situation is therefore the same as in long-chain polyphosphates. All tetrahedra of a cyclic anion are internal tetrahedra Phosphates with this type of anion were for a long time called metaphosphate. This term was unfortunately used to refer to both cyclic anion phosphates and long-chain polyphosphates, thus introducing further confusion in the field of condensed phosphates. Today, the term cyclophosphates is used.

**Table 8: Nomenclature used for cyclophosphates**

N	Anions	old nomenclature	existing nomenclature
3	$[P_3O_9]^{3-}$	Trimetaphosphates	Cyclotriphosphates
4	$[P_4O_{12}]^{4-}$	Tetrametaphosphates	Cyclotetraphosphates
5	$[P_5O_{15}]^{5-}$	Pentametaphosphates	Cyclopentaphosphates
6	$[P_6O_{18}]^{6-}$	Hexametaphosphates	Cyclohexaphosphates
8	$[P_8O_{24}]^{8-}$	Octométaphosphates	Cyclooctophosphates
9	$[P_9O_{27}]^{9-}$	Nonamétaphosphates	Cyclononaphosphates
10	$[P_{10}O_{30}]^{10-}$	Decamétaphosphates	Cyclohexaphosphates
12	$[P_{12}O_{36}]^{12-}$	Dodécamétaphosphates	Cyclododécaphosphates

In the table we gather the different anionic formulas of the currently known cyclic anions and the corresponding terminology.

#### 1. $P_3O_9^{3-}$

In this part we present the synthesis of Diphosphates associated with manganese by the various synthetic methods, structural characterization thus studies by IR vibration spectrometry of their anions. We have been able to isolate and characterize several phosphates of  $Mn-P_3O_9$  type as an

example:  $MnNH_4P_3O_9$ ,  $MnBa_2(P_3O_9)_2 \cdot 6H_2O$ ,  $MnCa_2(P_3O_9)_2 \cdot 10H_2O$ ,  $MnSr_2(P_3O_9)_2 \cdot 4H_2O$ ,  $Mn(NH_4)_4(P_3O_9)_2 \cdot 6H_2O$ ,  $MnK_4(P_3O_9)_2$ ,  $Mn_3(P_3O_9)_2 \cdot 10H_2O$

### 5.2.1 Sample preparation

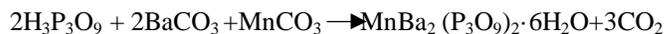
#### 1. $MnNH_4P_3O_9$

Ammonium polyphosphate ( $(NH_4PO_3)_n$ , n ~ 700, Exolit 422 from Hoechst) and manganese dioxide ( $MnO_2$ , Russian standard GOST 4470-79, Khimreaktiv) were used. Weight ratios of 3:1 and 6:1 for APP/ $MnO_2$  respectively were chosen for detailed study, as the flame retardant additive APP +  $MnO_2$  showed maximum efficiency in combustion tests in air and in synthetic oxygen/nitrogen atmospheres (oxygen index test), at these ratios.

Chemical interaction in the APP/ $MnO_2$  systems at high temperature was studied by thermogravimetry (TG) using a Mettler TA 3000 thermal analyzer. Experiments were carried out at a heating rate of 10 K  $min^{-1}$  in an argon flow of 100  $cm^3 min^{-1}$ . Ceramic holders with which APP and  $MnO_2$  do not react were used [27].

#### 2. $MnBa_2(P_3O_9)_2 \cdot 6H_2O$

Single crystals of  $MnBa_2(P_3O_9)_2 \cdot 6H_2O$  have been prepared by adding slowly dilute cyclotriphosphoric acid to an aqueous solution of barium carbonate and manganese carbonate with a stoichiometric ratio Ba/Mn=2, according to the following chemical reaction:



The so-obtained solution is then slowly evaporated at room temperature until large rectangular prisms of  $MnBa_2(P_3O_9)_2 \cdot 6H_2O$  are obtained. The crystals are stable in air for many months under normal conditions of temperature and hygrometry [28].

#### 3. $MnCa_2(P_3O_9)_2 \cdot 10H_2O$ and $MnCa_2(P_3O_9)_2$

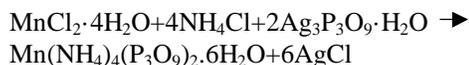
$MnCa_2(P_3O_9)_2$  was obtained by Tridane [3] by total dehydration of  $MnCa_2(P_3O_9)_2 \cdot 10H_2O$  under atmospheric pressure between 400 and 450°C.  $MnCa_2(P_3O_9)_2$  [3] was prepared, otherwise, using the method of Thilo and Grunze [10]. Stoichiometric quantities of  $(NH_4)_2HPO_4$ ,  $MnCO_3$  and  $CaCO_3$  are well ground and mixed, and very progressively heated to 150–200°C to expel ammonia and water vapor. The heating is then resumed up to 450°C, and this temperature is maintained with intervening grindings until a pure phase is obtained, as checked by X-ray diffraction.  $MnCa_2(P_3O_9)_2$  was obtained as polycrystalline samples [29].

#### 4. $\text{MnSr}_2(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$

The fourth example of cyclotriphosphates, described in this study, with a general formula  $\text{M}^{\text{II}}\text{M}^{\text{II}}_2(\text{P}_3\text{O}_9)_2 \cdot n\text{H}_2\text{O}$  is  $\text{MnSr}_2(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ . This cyclotriphosphate has no isotopic compound. An automatic indexation using the Treor program and Dicvol 91 program showed that  $\text{MnSr}_2(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  crystallizes in the triclinic system with  $M(20)=29.6$  and  $F(30)=34.4$ . The weight loss performed by slowly heating up to a temperature of  $400^\circ\text{C}$ , confirms the compound as a tetrahydrate. Infrared, Raman and non-linear optical studies show that this salt is centrosymmetric. So, the space group of  $\text{MnSr}_2(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  is P-1 and its main crystallographic features are reported in Table1. Single crystals of  $\text{MnSr}_2(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  cannot be obtained. Only polycrystalline samples can be prepared by the method of ion-exchange resin ‘‘Amberlite IR 120’’ [30].

#### 5. $\text{Mn}(\text{NH}_4)_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$

$\text{Mn}(\text{NH}_4)_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$  is isotopic of four cyclotriphosphates:  $\text{ZnK}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$  [14],  $\text{CoRb}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiRb}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnRb}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$ . This compound was prepared using silver cyclotriphosphate monohydrate as starting material. An aqueous solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}$  in stoichiometric proportions is added with the corresponding amount of  $\text{Ag}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$ , according to the following chemical reaction:



After filtration, to eliminate the insoluble silver chloride, the resulting solution is kept at room temperature until the formation of  $\text{Mn}(\text{NH}_4)_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$  as polycrystalline samples [31].

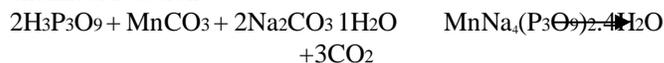
#### 6. $\text{MnK}_4(\text{P}_3\text{O}_9)_2$

$\text{CdK}_4(\text{P}_3\text{O}_9)_2$ ,  $\text{MnK}_4(\text{P}_3\text{O}_9)_2$  and  $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$  are isotopic of a series of five cyclotriphosphates corresponding to the general formula  $\text{M}^{\text{II}}\text{TL}_4(\text{P}_3\text{O}_9)_2$  ( $\text{M}^{\text{II}} = \text{Mg}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Ca}^{2+}$ ), of  $\text{MnTL}_4(\text{P}_3\text{O}_9)_2$  and also of  $\text{MnCa}_2(\text{P}_3\text{O}_9)_2$  described in the present study. The five cyclotriphosphates described above were discovered during the elaboration of various  $\text{TIPO}_3\text{-M}^{\text{II}}(\text{PO}_3)_2$  phase-equilibrium diagrams where they always appear as noncongruent melting compounds. Rakotomahanina-Rolaisoa proposed a model for this atomic arrangement using the magnesium thallium cyclotriphosphate,  $\text{MgTL}_4(\text{P}_3\text{O}_9)_2$ .  $\text{CdK}_4(\text{P}_3\text{O}_9)_2$  was obtained by total dehydration of  $\text{CdK}_4(\text{P}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$  under atmospheric pressure between 200 and  $550^\circ\text{C}$ .  $\text{MnK}_4(\text{P}_3\text{O}_9)_2$  was obtained by total dehydration of  $\text{MnK}_4(\text{P}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$  under atmospheric pressure between 200 and  $550^\circ\text{C}$ . It is worth noticing that  $\text{MnK}_4(\text{P}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$  is the isotopic of the corresponding cadmium salt,  $\text{CdK}_4(\text{P}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$ , whose chemical preparation and crystal structure have been reported

by M.T. Averbuch-Pouchot.  $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$  was obtained by total dehydration of  $\text{NiRb}_4(\text{P}_3\text{O}_9)_2 \cdot 2\text{H}_2\text{O}$  under atmospheric pressure between 300 and  $400^\circ\text{C}$ . Additional materials as indexing X-ray diffraction patterns of the eight condensed phosphates studied in the present work can be obtained on request to the Moroccan author [31].

#### 7. $\text{MnNa}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ - $\text{MnNa}_4(\text{P}_3\text{O}_9)_2$

Crystals of the title compound were prepared by adding slowly dilute cyclotriphosphoric acid to an aqueous solution of manganese carbonate and sodium carbonate with a stoichiometric ratio Na/Mn D 4, according to the following chemical reaction:



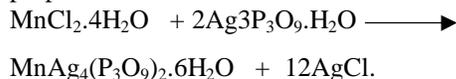
The so-obtained solution was then slowly evaporated at room temperature until polycrystalline samples of  $\text{MnNa}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  were obtained. The cyclotriphosphoric acid used in this reaction was prepared from an aqueous solution of  $\text{Na}_3\text{P}_3\text{O}_9$  passed through an ion-exchange resin ‘‘Amberlite IR 120’’ 16  $\text{Na}_3\text{P}_3\text{O}_9$  was obtained by thermal treatment of sodium dihydrogenomonophosphate, at  $530^\circ\text{C}$  for 5 h in air according to:



The weight loss performed by slowly heating up to a temperature of  $300^\circ\text{C}$ , confirms the compound as a tetrahydrate,  $\text{MnNa}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ .  $\text{MnNa}_4(\text{P}_3\text{O}_9)_2$  was obtained as polycrystalline samples by total dehydration of  $\text{MnNa}_4(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$  under atmospheric pressure between 300 and  $600^\circ\text{C}$  [32].

#### 8. $\text{MnAg}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$

Polycrystalline samples of  $\text{MnAg}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$  were prepared by the metathesis reaction of Boule (Boule 1938) using silver cyclotriphosphate monohydrate as starting material. An aqueous solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  is added with the corresponding amount of  $\text{Ag}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$  in stoichiometric proportions. The reaction scheme is the following:

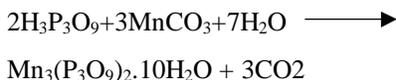


To eliminate the insoluble silver chloride, the resulting solution after filtration is kept at room temperature until the formation of polycrystalline samples of  $\text{MnAg}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$ . The weight loss performed by slowly heating up to a temperature of  $350^\circ\text{C}$  confirms the compound as a hexahydrate. The polycrystalline samples are stable in air for many months under normal conditions of temperature and hygrometry [33].

## 9. $\text{Mn}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$

.....

Polycrystalline samples of the title compound,  $\text{Mn}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$  [34], were prepared by adding slowly dilute cyclotriphosphoric acid to an aqueous solution of manganese carbonate, according to the following chemical reaction:



The so-obtained solution was then slowly evaporated at room temperature until polycrystalline samples of  $\text{Mn}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$  were obtained. The cyclotriphosphoric acid 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 "Amberlite IR 120" [35].

### 5.2.2 Sample characterization

#### 1. X-ray powder diffraction

The calculation of the parameters and the analysis of the X-ray diffractogram enabled us to verify the purity of the synthesized product. The unit-cell parameters of these triphosphates are collected in table 9.

**Table 9:** Main Crystallographic Data for the cyclotriphosphate associated to manganese.

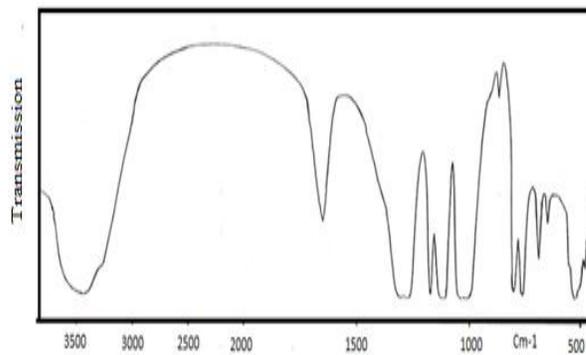
Formula	a(Å) $\alpha(^{\circ})$	b(Å) $\beta(^{\circ})$	c(Å) $\gamma(^{\circ})$	S.G.	Z	References
$\text{MnNH}_4\text{P}_3\text{O}_9$	7.357	12.186	9.390	Pmcm	4	[27]
$\text{MnBa}_2(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$	7.534 107.93	11.898 100.36	13.053 95.78	P-1	4	[28]
$\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$	9.631	18.173 109.44	7.976	P2 <sub>1</sub> /n	2	[29]
$\text{MnCa}_2(\text{P}_3\text{O}_9)_2$	7.392	7.392	20.134	P-31c	2	[29]
$\text{MnSr}_2(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$	6.653 103.37	7.110 95.81	5.123 93.04	P-1	1	[30]
Mn $(\text{NH}_4)_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$	13,178	11,030 126.76	9,965	C2/m	2	[31]
$\text{Mn}_3(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$	9.631	18,173 109,438	7,976	P2 <sub>1</sub> /n	2	[34]

### 2. Characterization by infrared vibration spectrometry of cyclotriphosphate decahydrate of manganese and dicalcium, $\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$

The packaging used for all spectra of infrared absorption is the same: 1 mg of product in 200 mg of KBr intimately crushed for the manufacture of a pellet at room temperature and at atmospheric pressure.

The absorption spectrum IR of  $\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$  [36] (Figure 4) contains:

- In the spectral region  $4000\text{-}3000\text{ cm}^{-1}$ , characteristic of OH valence bands, a single wideband around  $3450\text{ cm}^{-1}$  accompanied by a shoulder at  $3290\text{ cm}^{-1}$ .
- In the range,  $1700\text{-}1600\text{ cm}^{-1}$  characteristic of water deformation bands, a strong intensity band at  $1671\text{ cm}^{-1}$ , accompanied by a shoulder at  $1690\text{ cm}^{-1}$ .
- between  $1400$  and  $640\text{ cm}^{-1}$ , the characteristic domain of the valence bands of the  $\text{P}_3\text{O}_9^{3-}$  cycle, possibly of the water-cycle interaction and rotations of the water molecules, seven bands are observed. Four broad bands of high intensity all appear as a doublet of frequency: ( $1280, 1264\text{ cm}^{-1}$ ), ( $1132, 1105\text{ cm}^{-1}$ ), ( $1025, 987\text{ cm}^{-1}$  and ( $791, 753\text{ cm}^{-1}$ ). All the other bands are fine and of average intensity, one appears doubled at  $685\text{ cm}^{-1}$ - $645\text{ cm}^{-1}$  and two others are observed at  $1162\text{ cm}^{-1}$  and  $868\text{ cm}^{-1}$ . The symmetry of the  $\text{P}_3\text{O}_9^{3-}$  ring in this compound is lower than the symmetry C3h or D3h .
- Between  $640$  and  $400\text{ cm}^{-1}$ , the domain characterizing the deformation vibrations of oxygenates outside the cycle ( $\delta\text{OPO}^+\delta\text{POP}$ ) exist two frequencies respectively located at  $522\text{ cm}^{-1}$  and  $476\text{ cm}^{-1}$ .



**Figure 4:** IR absorption spectrum of  $\text{MnCa}_2(\text{P}_3\text{O}_9)_2 \cdot 10\text{H}_2\text{O}$

#### 2. $\text{P}_4\text{O}_{12}$

### 5.2.3 Sample preparation

#### 1. $\text{Mn}_2\text{P}_4\text{O}_{12}$

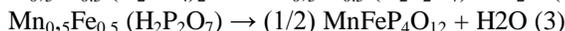
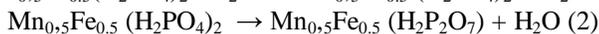
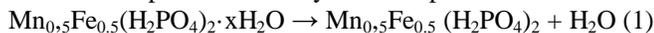
The total dehydration of  $\text{Mn}(\text{NH}_4)_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$  [37] leads at  $500^{\circ}\text{C}$  to the anhydrous form, cyclotetraphosphate  $\text{Mn}_2\text{P}_4\text{O}_{12}$ . It's the first time that the dehydration and the calcination of a cyclotriphosphate ( $\text{P}_3\text{O}_9$ ) leads to a cyclotetraphosphate ( $\text{P}_4\text{O}_{12}$ ),  $\text{Mn}_2\text{P}_4\text{O}_{12}$  [37, 38] (figure 5).

#### 2. $\text{MnFeP}_4\text{O}_{12}$

The binary  $\text{Mn}_{0.5}\text{Fe}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  compound was prepared by solution precipitation method using the metal sources of Mn(c; complexometric) (99.99%, Merck), Fe (c; complexometric), (99.99%, Fluka) and phosphoric acid (86.4% (w/w)  $\text{H}_3\text{PO}_4$ , Merck) as starting materials. In typical procedure, 0.5494 g of Mn(c) and 0.5593 g of Fe(c) were

dissolved in 70% H<sub>3</sub>PO<sub>4</sub> (81.02 mL of 86.4% (w/w) H<sub>3</sub>PO<sub>4</sub> in 18.98 mL of water) with continuous stirring at ambient temperature. The resulting solution was stirred until H<sub>2</sub> (g) was completely evolved (15–30 min) and the nearly dry precipitates were obtained, then 10 mL of acetone was added to allow highly crystalline product to be developed. The prepared solid was filtered by suction pump, washed with acetone and dried in air. The manganese and iron contents of Mn<sub>0.5</sub>Fe<sub>0.5</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O compound were determined by dissolving in 0.0126 M hydrochloric acid using atomic absorption spectrophotometry (AAS, Perkin–Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. The water content was determined by heating at 500 C in the furnace for 3 h and the manganese iron cyclo-tetraphosphates (MnFeP<sub>4</sub>O<sub>12</sub>) were obtained as the final decomposition yield [39].

This process formally could be presented as:



## 5.2.4 Sample characterization

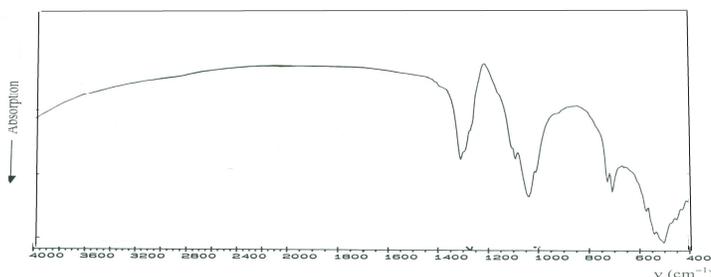
### 1. X-ray powder diffraction

The calculation of the unit-cell parameters and the analysis of the X-ray diffraction patterns enabled us to verify the purity of the synthesized product Mn<sub>2</sub>P<sub>4</sub>O<sub>12</sub>. The unit-cell parameters of these cycloriphosphates are collected in table 10.

**Table 10:** Main Crystallographic Data for the Cyclotetraphosphates associated with manganese.

Formula	a(Å) α(°)	b(Å) β(°)	c(Å) γ(°)	S.G.	Z	References
Mn <sub>2</sub> P <sub>4</sub> O <sub>12</sub>	11.883	8.588 119.21	10.137	C2/c	4	[37, 38]
MnFeP <sub>4</sub> O <sub>12</sub>	12.06	8.48 119.12	10.12	C2/c	4	[39]

### 2. Characterization of P<sub>4</sub>O<sub>12</sub><sup>4-</sup> in Mn<sub>2</sub>P<sub>4</sub>O<sub>12</sub> by IR vibration spectrometry



**Figure 5:** IR absorption spectrum of Mn<sub>2</sub>P<sub>4</sub>O<sub>12</sub>

**Table 11:** Characterization of P<sub>4</sub>O<sub>12</sub><sup>4-</sup> by IR vibration

Frequencies (cm <sup>-1</sup> )	Vibrations
1315	ν <sub>as</sub> OPO <sup>-</sup>
1301	
1275	ν <sub>s</sub> OPO <sup>-</sup>
1116	
1101	
1048	
1017	ν <sub>as</sub> POP
733	
712	ν <sub>s</sub> POP
669	

### spectrometry

### 3. P<sub>6</sub>O<sub>18</sub><sup>6-</sup>

Mn<sub>3</sub>P<sub>6</sub>O<sub>18</sub>.6H<sub>2</sub>O [40] was prepared by reaction of Ag<sub>6</sub>P<sub>6</sub>O<sub>18</sub> with MnCl<sub>2</sub>. It crystallizes in the rhombohedral space group R3 with Z=2.

**Table 12:** Main Crystallographic Data for the

Formula	a(Å) α(°)	b(Å) β(°)	c(Å) γ(°)	S.G.	Z	References
Mn(PO <sub>3</sub> ) <sub>3</sub>	9.703	10.667	6.362	Pnma	4	[42]
MnBa(PO <sub>3</sub> ) <sub>4</sub>	14.69	9,147 90,57	7,201	P2 <sub>1</sub> /n	4	[43]
Li <sub>2</sub> Mn(PO <sub>3</sub> ) <sub>4</sub>	9.4295	9.2755	10.0972	Pnma	4	[44]
(NH <sub>4</sub> ) <sub>2</sub> Mn(PO <sub>3</sub> ) <sub>4</sub>	11.30	12,99 101.5	7,839	P2 <sub>1</sub> /n	4	[45]
Cs <sub>2</sub> Mn(PO <sub>3</sub> ) <sub>4</sub>	7.9762	13,24.91 101,97	11,5462	P2 <sub>1</sub> /n	4	[46]
Mn <sub>2</sub> (O <sub>3</sub> P–C <sub>4</sub> H <sub>2</sub> S–PO <sub>3</sub> ) <sub>2</sub> H <sub>2</sub> O	11.60	4,943 107.22	19.614	P2	4	[47]
MnNH <sub>4</sub> (PO <sub>3</sub> ) <sub>3</sub>	6,771	6,771	10,026	P-6c2	4	[48]
LiMn(PO <sub>3</sub> ) <sub>3</sub>	8.364	8.561 101.4	8.6600	P2 <sub>1</sub>	4	[49]

### Cyclohexaphosphates associated to manganese

### 5.3 Long chain polyphosphates (PO<sub>3</sub>)<sub>n</sub>

#### 5.3.1 Sample preparation

##### 1. Mn(PO<sub>3</sub>)<sub>3</sub>

The method of preparation used consists of heating a mixture of manganese carbonate in an excess of orthophosphoric acid to 450-500

C for one fi three days at the concentration (1 mol of MnCO<sub>3</sub> for 5 fi 15 mol of H<sub>3</sub>PO<sub>4</sub>).

The crystals have a characteristic red-violet colour that clearly distinguishes them from bivalent manganese téramétaphosphate, which is a pale pink colour (Beucher & Grenier 1968). Both types of compote can crystallize at the same time. Their crystalline morphology is also different: the Manganous salts appear as octahedrons or needles growing in dendrites, the Manganous salts as prisms ( It

should be noted that if orthophosphoric acid is replaced by diammonium phosphate only the latter crystallises, the medium not being sufficiently acidic to stabilise the manganic salts) [42].

## 2. BaMn(PO<sub>3</sub>)<sub>4</sub>

These four salts are easily prepared by calcination of a mixture in stoichiometric proportions of diammonium monophosphate, barium carbonate and bivalent metal carbonate corresponding to the different formulae of the compounds. The heating temperatures are 700 °C for MnBa(PO<sub>3</sub>)<sub>4</sub>, CdBa(PO<sub>3</sub>)<sub>4</sub> and CaBa(PO<sub>3</sub>)<sub>4</sub> and 400 °C for HgBa(PO<sub>3</sub>)<sub>4</sub> [43].

## 3. Li<sub>2</sub>Mn(PO<sub>3</sub>)<sub>4</sub>

The polyphosphate Li<sub>2</sub>Mn(PO<sub>3</sub>)<sub>4</sub> was synthesised and its structure characterized from powder diffraction data by Averbuch-Pouchot & Durif [J. Appl. Cryst. (1972), 5, 307–308]. These authors showed that the structure of this phosphate is isotypic to that of Li<sub>2</sub>Cd(PO<sub>3</sub>)<sub>4</sub>, as confirmed by the present work. The structure is built from infinite zigzag polyphosphate chains, [(PO<sub>3</sub>)], extending along [010]. These polyphosphate chains are connected by sharing vertices with MnO<sub>6</sub> octahedra (site symmetry *m*.) and Li<sub>2</sub>O<sub>7</sub> polyhedra, which form also chains parallel to [010]. Adjacent chains are linked by common vertices of polyhedra in such a way as to form porous layers parallel to (100). The three-dimensional framework delimits empty channels extending along [010] [44].

## 3. Mn(NH<sub>4</sub>)<sub>2</sub>(PO<sub>3</sub>)<sub>4</sub>

The preparation of all these compounds can be schematized by the following reaction:



The method used is to take a very large excess of diammonium phosphate and heat the mixture 350 °C for one day. Crystals are obtained in the form of bipyramidal prisms with an almost square cross-section; the axis of the prism corresponds to the *c*-direction of the monoclinic unit cell. Chromatographic analysis shows that they are long chain polyphosphates [45].

## 4. Cs<sub>2</sub>Mn(PO<sub>3</sub>)<sub>4</sub>

5. As starting compounds were Cs, CO, MnO and H<sub>3</sub>PO<sub>4</sub> (85%), all p. a. Merck, used. Weighed quantities of the starting compounds, corresponding to a molar ratio Cs: Mn: P = 3: 1: 5, were left for 7 days at 500 °C in an open porcelain crucible. The by-product resulting, in contrast to Cs<sub>2</sub>Mn(PO<sub>3</sub>)<sub>4</sub>, water-soluble (CsPO<sub>3</sub>), was separated by leaching (ultrasonic bath, 35 kHz, 30 min.) with water from the reaction product. After filtration and washing we obtained a blue powder, already for an X-ray structure analysis contained suitable single crystals [46].

## 6. Mn<sub>2</sub>(O<sub>3</sub>P–C<sub>4</sub>H<sub>2</sub>S–PO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O

7. Hydrothermal Synthesis of Mn<sub>2</sub>(O<sub>3</sub>P–C<sub>4</sub>H<sub>2</sub>S–PO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O  
3. Thiophene-2,5-diphosphonic acid 2 (0.05 g, 0.2 mmol), urea (0.024 g, 0.4 mmol), and Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.118 g, 0.4 mmol) were dissolved in distilled water (15 mL). The resulting solution was placed in a PTFE insert of 50 mL. After stirring 15 min the pH of the mother solution (pH<sub>initial</sub>) was 1.66. The insert was then transferred in a Berghof pressure digestion vessel and heated from room temperature to 140 °C in 20 h, heated 40 h at 140 °C, and cooled to room temperature in 40 h. At the opening of the PTFE insert the pH of the solution (pH<sub>final</sub>) was 4.13, and the final material, obtained as light brown crystals with suitable size for structure resolution on a single crystal, was isolated by filtration, washed with water rinsed with absolute ethanol, and dried in air [47].

### 5.3.2 Sample characterization

#### 1. X-ray powder diffraction

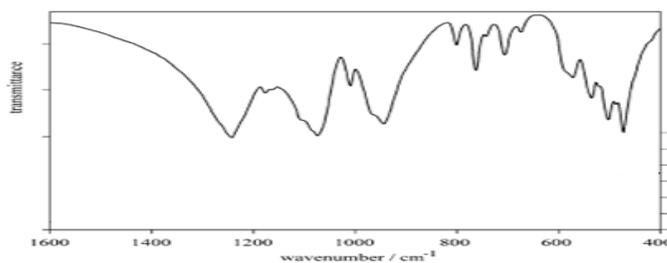
The calculation of the unit-cell parameters and the analysis of the X-ray diffractogram enabled us to verify the purity of the synthesized product. The mesh parameters of these Triphosphates are collected in table 13

**Table 13:** Main Crystallographic Data for the polyphosphates associated to manganese.

Formula	a(Å) α(°)	b(Å) β(°)	c(Å) γ(°)	S.G.	Z	References
Mn <sub>3</sub> P <sub>6</sub> O <sub>18</sub> ·6H <sub>2</sub> O	14,836	14,836	15,781	R-3	2	[40]
Cs <sub>3</sub> Cd <sub>3</sub> Mn(P <sub>6</sub> O <sub>18</sub> ) <sub>2</sub>	16.201	10.033 127,10	12.540	C2/m	2	[41]
Cs <sub>3</sub> Zn <sub>3</sub> Mn(P <sub>6</sub> O <sub>18</sub> ) <sub>2</sub>	16.092	9,832 127,288	12.304	C2/m	2	[41]

S.G. Space Group

#### 2. Characterization of P<sub>3</sub>O<sub>9</sub> in Mn(PO<sub>3</sub>)<sub>3</sub> by IR vibration spectrometry.



**Figure 6:** IR absorption spectrum of MnNi(PO<sub>3</sub>)<sub>3</sub>

Figure 6 shows the IR spectrum of the title compound MnNi(PO<sub>3</sub>)<sub>3</sub>. The IR spectrum of catena-polyphosphates is not significantly different from those of catena-oligophosphates. The only characteristic bands should be found in the region between 800 and 650 cm<sup>-1</sup>, where the number of bands should correspond to the periodicity of the phosphate chain. Unfortunately, this holds quite reliably only for low chain periodicities. In Mn(PO<sub>3</sub>)<sub>2</sub>, the characteristic frequencies of catena-polyphosphate chains such as the vas(PO<sub>2</sub>) are detected between 1200 and 1310 cm<sup>-1</sup> with a

maximum at  $1243\text{ cm}^{-1}$ , the very intense vas(POP) at  $944\text{ cm}^{-1}$  and  $\nu(\text{PO term})$  ranging from  $1019$  up to  $1100\text{ cm}^{-1}$ . Thus the observed vibrational data are in good agreement with the expected values [50]. It is worth noticing that long chain polyphosphates are good corrosion inhibitors [51-55].

## 6. CONCLUSION

We have collected crystallographic data for manganese-associated condensed phosphates and monophosphates with known structures. Various condensed phosphates and monophosphates, especially anions, have been characterized by infrared vibration spectrometry. Different methods for the preparation of condensed phosphates have been cited here (classical methods, thermal methods, Boule process, flow methods and ion exchange resins). And also, we have collected crystallographic data for condensed phosphates and monophosphates associated to strontium with known structures. Until today there are no condensed phosphates studied with the following anions: cyclophosphates  $\text{P}_n\text{O}_{3n}^{n-}$  (3 types of anions:  $\text{P}_5\text{O}_{15}^{5-}$ ,  $\text{P}_8\text{O}_{24}^{8-}$ ,  $\text{P}_{12}\text{O}_{36}^{12-}$ ) and oligophosphates  $(\text{P}_n\text{O}_{3n+1})^{(n+2)-}$  (3 types of anions:  $\text{P}_3\text{O}_{10}^{5-}$ ,  $\text{P}_4\text{O}_{13}^{6-}$ ,  $\text{P}_5\text{O}_{16}^{7-}$ ).

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