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RESEARCH ARTICLE

CHEMICAL PREPARATIONS, CRYSTAL DATA FOR MONOPHOSPHATES AND CONDENSED PHOSPHATES ASSOCIATED TO BARIUM AND IR STUDIES OF THEIR ANIONS.

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Abstract

Monophosphates and condensed phosphates associated to barium, the subject of this paper, constitute an important part of phosphate chemistry and have been subject to many studies and applications in many fields of research on materials and industry. In order to collect unit-cell parameters of these compounds, establish a data bank of formula existing till now and to have an idea about facilities and difficulties on their preparations, we focus the present research on chemical preparations, crystal data and IR studies for condensed phosphates and monophosphates. The present work reports the chemical preparations, main crystallographic data for condensed phosphates and monophosphates associated to barium and characterization by infrared vibration spectrometry for anions, PO^{3-} in $Ba(PO_3)_2$, PO_4^{3-} in $Ba_3(PO_4)_2$, $P_2O_7^{4-}$ in $BaMnP_2O_7$, $P_3O_9^{3-}$ in $Ba_3(P_3O_9)_2.6H_2O$, $P_4O_{12}^{4-}$ in $Ba_2P_4O_{12}.4H_2O$, $P_6O_{18}^{6-}$ in $Ba_3P_6O_{18}.8H_2O$ and $P_{10}O_{30}^{10-}$ in $Ba_2ZnP_{10}O_{30}$.

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Introduction:-

This class of phosphates, condensed phosphates and monophosphates, developed over a long period of time and, even today, is still relatively poor understood as compared with condensed silicates, germinates and vanadates. More than four hundred and fifty different types of atomic arrangements are today well established in the field of condensed phosphates and monophosphates. In most cases, dealing with these structure determinations report a detailed description of one atomic arrangement but pay little attention to the existence or the possible existence of isotypic compounds and others. In a domain one can consider now as deeply investigated and where sufficient basic data have been accumulated, this situation has several disadvantages; it favors duplicate structural papers and discourages any attempts to establish correlations in a given region of condensed phosphates and monophosphates chemistry. The present work describes the chemical preparations and reports crystal data for condensed phosphates and monophosphates associated to barium and IR vibration spectrometry studies of their anions.

Infrared Vibration Spectrometry

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

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Elaboration And Crystal Data

First let us try to explain what we commonly call a phosphate. A general and rather abstract definition can be given by saying that phosphates are salts of both the monophosphoric acid H_3PO_4 and its various condensed or polymeric forms. The corresponding anions have varied geometries but one common feature: they are all built up by pentavalent phosphorus atoms surrounded by more or less distorted tetrahedra made of four oxygen atoms. In a very elementary way, one can roughly classify phosphates into three main groups : monophosphates $(PO_4)^{3-}$, (O / P = 4), oxyphosphates $(O(PO_4))^{5-}$ (O / P > 4) and condensed phosphates (O / P < 4) (cyclophosphates $(P_nO_{3n})^{n-}$ n = 3, 4, 5, 6, 8, 9, 10 and 12; oligophosphates $(P_nO_{3n+1})^{(n+2)-}$ n = 2, 3, 4 and 5; long chain polyphosphates $(PO_3)_n^{-}$ n = 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, ∞ and ultraphosphates $(P_{n+2}O_{3n+5})^{n-}$ n = 2, 3, 4 and 6.

Monophosphates PO_4^{3-}

α-$BaHPO_4$

The synthesis of **α** -$BaHPO_4$[1] was performed in a Petri dish according to the following chemical reaction:

$$4Ba(OH)_2 + P_4O_{10} \longrightarrow 4\alpha\text{ - }BaHPO_4 + 2H_2O \quad (1)$$

51.4 mg (0.300 mmol) of barium hydroxide $Ba(OH)_2$ were dissolved in a Petri dish with 10 ml of water and 21.3 mg (0.150 mmol) of phosphorus pentoxide P_2O_5 were added to the solution. The covered Petri dish was put into a compartment drier at 200°C until the water was evaporated (2 days). The reaction yielded single-phase α-$BaHPO_4$ as a crystalline, colourless and non hygroscopic powder.

$KBaPO_4$

Arcanite type $KBaPO_4$ single crystals may be obtained by either of the following chemical reactions, at 650°C [2]:

$$K_3PO_4 + BaF_2 \longrightarrow KBaPO_4 + 2KF$$

$$K_4P_2O_7 + BaF_2 \longrightarrow KBaPO_4 + KPO_3 + 2KF$$

$Ba_3(PO_4)_2$

Mixtures of reagent-grade $BaCO_3$ and $NH_4H_2PO_4$ corresponding to the chemical compositions of $Ba_3(PO_4)_2$ is prepared. It is calcined at about 1000°C. After grinding the calcined products into powder, it is pressed into pellets and heated again at 1400°C for 40 hours. Then, the sample is slowly cooled to 1250°C and kept at that temperature for over 4 days [3].

$BaCo_2(PO_4)_2$

Single crystals of $BaCo_2(PO_4)_2$ were prepared from a mixture of $BaCO_3$ (1.375g), $CoBr_2$ (1.523g), 85% H_3PO_4 (3.33g), guanidinium carbonate $\{(C(NH_2)_3)_2CO_3$; 1.254g$\}$ and H_2O (10 ml). These components were sealed in a 23 ml teflon-lined hydrothermal bomb and heated to 180 °C for 3 days. After cooling to ambient temperature over several hours, pink crystals of the title compound were recovered by vacuum filtration and drying in air [4].

$BaCu_2(PO_4)_2$

$BaCu_2(PO_4)_2$ has been prepared by heating a mixture of $(NH_4)_2HPO_4$, $BaCO_3$ and CuO in the molar ratio 2:1:2. The reaction is carried out in a platinum crucible. The mixture, after being ground, is slowly heated to 1000°C and cooled to 800°C with a cooling rate of 5°C/h. Then the product was put in the furnace and cooled down to room temperature. By this procedure single crystals of $BaCu_2(PO_4)_2$ have been isolated [5].

$Ba(H_2PO_4)_2$

Barium phosphate was prepared as previously reported [6]. Briefly, to a dilute solution of barium chloride diehydrate was slowly added a 1.50 mol dm^{-3} dibasic ammonium phosphate solution and the mixture was heated to 180 °C. The suspension formed was stirred for 1 h, when the solid started to settle out. The solid was filtered and dried under vacuum at 50 °C. Finally, the resulting compound was heated at 440 K for 48 h to eliminate ammonia.

$KBaFe_2(PO_4)_3$

A polycrystalline sample of $KBaFe_2(PO_4)_3$ was prepared by heating a stoichiometric mixture of potassium and barium carbonates, ferric oxide and ammonium dihydrogen phosphate for 72 hours at a temperature of 1100°C in a platinum crucible [7].

$KBaCr_2(PO_4)_3$

A polycrystalline sample of $KBaCr_2(PO_4)_3$ was prepared by heating a pelleted stoichiometric mixture of barium carbonate, chromium sesquioxide, diammonium hydrogen phosphate and potassium carbonate at a temperature of 1100°C in a platinum crucible for several weeks, with intermediate grinding and pelleting. Initially, the furnace temperature was raised from 80 to 1100°C at a rate of 300°C per hour, and the final cooling was at a rate of 50°C per hour. The product was a green, poorly sintered pellet (heating at 1200°C did not significantly increase the degree of sintering) [8].

Table 1:-Main Crystallographic Data for the monophosphates associated to barium.

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	S.G.	Z
α- $BaHPO_4$	4.5996	22.809	14.081	Aem2	16
$Ba_3(PO_4)_2$	5.6038	5.6038	21.000	R-3m	1
$BaCo_2(PO_4)_2$	4.8554	4.8554	23.215	R-3	3
$BaCu_2(PO_4)_2$	9.226 106.76	9.271 101.69	10.516 115.70	P-1	4
$BaKCr_2(PO_4)_3$	9.789	9.789	9.789	$P2_13$	4
$BaKFe_2(PO_4)_3$	9.8732	9.8732	9.8732	$P2_13$	4
$BaKPO_4$	7.709	5.663 128.14	9.972	Pnma	4
$Ba(HPO_4)_2$	10.273	7.803	8.566	Pccn	4

Characterization of PO_4^{3-} in $Ba_3(PO_4)_2$by IR vibration spectrometry.
The IR absorption spectrum of $Ba_3(PO_4)_2$ is reported in Fig 1.

The ion PO_4^{3-}, with tetraedric symmetry, contained in monophosphates has two types of vibrations : valence P-O (P-O bond : valence vibration PO) and deformation O-P-O (O-P-O angle : bending vibration OPO). The PO valence vibrations (P-O bonds) are located about 1140 cm^{-1} (ν_3 : asymmetric stretching) and about 950 cm^{-1} (ν_1 : symmetric stretching). The OPO bending vibrations (OPO angles) are located about 490 cm^{-1} (ν_4: asymmetric deformation) and 360 cm^{-1} (ν_2 : symmetric deformation). Ion stretching frequencies $(PO_4)^{3-}$ are primarily determined by the fact that only one of P-O bond (P-O internal P-Oi and P-O external P-Oex) type is present in the PO_4^{3-} ion (P-O ex) in the structural unit. The number and frequency band allocation can be quite different as a result of the symmetry of the crystal (overall symmetry of the crystal cell and the local symmetry of the PO_4^{3-} ion). The nature of the vibration corresponding to the different observed bands in the spectrum of $Ba_3(PO_4)_2$ (Fig. 1) is given in Table 2.

Wave number (cm^{-1})

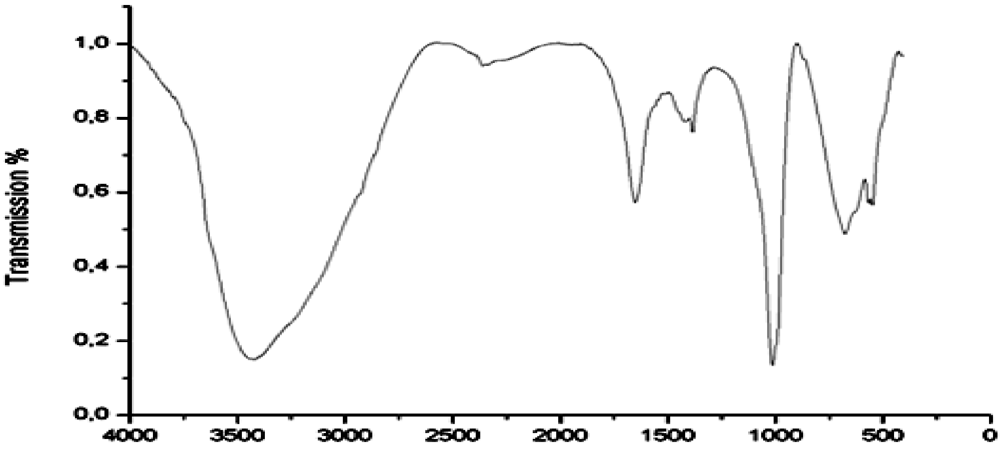


Figure 1:-IR spectra of the phosphate $Ba_3(PO_4)_2$

Table 2:-Frequencies (cm^{-1}) of IR absorption bands for $Ba_3(PO_4)_2$

Frequencies (cm^{-1})	Vibrations
3434 2346	ν O-H

1641	δ(H-O-H)
1380	ν_{as} PO
1005	ν_s PO
674	δ_{as} OPO^-
555	δ_S OPO^-

Condensed phosphates

Oligophosphates $(P_nO_{3n+1})^{(n+2)-}$

$P_2O_7^{4-}$:

α-$Ba_2P_2O_7$

The crystals of α-$Ba_2P_2O_7$were synthesized by combining 0.17 g of $BaHPO_4$ and 0.05 g of $NH_4H_2PO_4$ with 0.4 ml of 1M$Ba(OH)_2$ solution in a sealed silver ampoule for 7–10 days at 500°C with a counter pressure of 19000 psi (131 MPa). The contents of the ampoule were washed with deionized water. Colorless needle shaped single crystals of α-$Ba_2P_2O_7$ were the minor product and colorlesspolyhedrally shaped crystals of $BaHPO_4$ were the major product [9].

$BaMnP_2O_7$ monoclinic (1)

A mixture of $BaCO_3$ (0.987 g, 5.00 mmol), MnO_2 (0.435 g, 5.00 mmol) and P_2O_5 (0.710 g, 5.00 mmol) were 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. An yellow crystal was cleaved from the bulk sample and analysed by singlecrystal diffraction. It was found to belong to the monoclinic crystalline system [10].

$BaMnP_2O_7$ triclinic (2)

A mixture of $BaCO_3$ (0.987 g, 5.00 mmol), MnO_2 (0.436 g, 5.01 mmol) and P_2O_5 (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 [10].

$BaMP_2O_7$ (M = Ni, Co, Cu, Cd, Zn, Mg)

Rioueta[11] describedthesynthesesoftwomixed diphosphates, $BaNiP_2O_7$ and $BaCoP_2O_7$, prepared from powders at 900 °C and 1100 °C respectively. The two compounds are isotypic. The reported atomic arrangement of the cobalt salt showed the existence of a layered structure. Some discrepancies in the thermal coefficients indicate that additional work is needed to confirm the proposed atomic arrangement. Incommensurability phenomena appear for the nickel salt. The chemical preparation and crystal structure of $BaCuP_2O_7$ were recently reported by Moqine et al. [12]. The crystal structures of $BaCdP_2O_7$ and $BaZnP_2O_7$ were performed by Murashova et al. [13]. In addition the authors reported crystal data for $BaCoP_2O_7$ and $BaNiP_2O_7$. Crystal structure determinations for $BaMgP_2O_7$ and $PbZnP_2O_7$ were performed by Murashova et al. [14]

$BaLi_2P_2O_7$

Liebertz and Stahr[15] described the chemical preparation of $BaLi_2P_2O_7$. By using the Czochralski method, they prepared crystals up to 30 mrn long. This salt melts congruently at about 1100 °C.

The Czochralski process is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium and gallium arsenide), metals (e.g. palladium, platinum, silver, gold), salts and synthetic gemstones. The process is named after Polish scientist Jan Czochralski,[16]

$Ti_2Ba(P_2O_7)_2$, $Mo_2Ba(P_2O_7)_2$ and $V_2Ba(P_2O_7)_2$

Wang and Hwu[17] prepared the titanium derivative by heating a mixture of P_2O_5, Ti and Ba_2TiO_4 in a molar ratio 2:1:4, at 900 °C for 72 h in an evacuated silica tube. This calcination is followed by a slow cooling (5°/h) to room temperature. The crystals obtained are gemlike navy blue. A crystal structure determination for this compound was reported by the authorsthe corresponding molybdenum and vanadium compounds were prepared and described by

Leclaire et al. [18] and Benhamada et al. [19] respectively. In both cases, the atomic arrangements are refined. The crystallographic data for the diphosphates associated to bariumis given in Table 3.

Table 3:-Main Crystallographic Data for the diphosphates associated to barium.

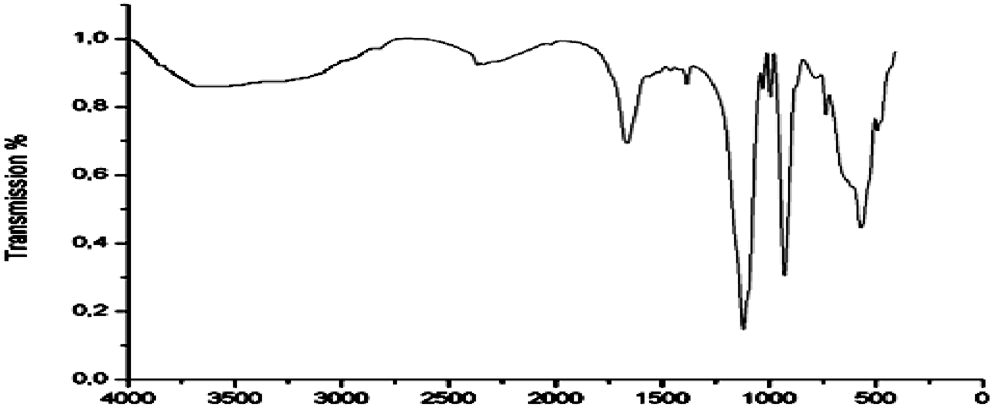
Formula	a(Å) α°	b(Å) β°	c(Å) γ°	S.G.	Z
α-$Ba_2P_2O_7$	9.2842	5.6113	13.796	Pnma	4
$BaMnP_2O_7$ (monoclinic)	12.825	8.633 90.08	5.5537	$P2_1/n$	2
$BaMnP_2O_7$ (triclinic)	5.473 102.10	7.593 86.03	7.166 89.29	P-1	2
$BaMgP_2O_7$	5.483	8.251 90.03	12.74	$P2_1/n$	4
$BaNiP_2O_7$	5.323 101.22	7.58 84.19	7.117 89.32	P-1	2
$BaCdP_2O_7$	5.641 78.55	7.038 89.83	7.624 86.79	P-1	2
$BaZnP_2O_7$	5.316 102.06	7.309 72.13	77.579 94.08	P-1	2
$BaCuP_2O_7$	7.353 90.83	7.578 95.58	5.231 103.00	P-1	2
$BaCoP_2O_7$	5.370 102.06	7.58 85.31	7.151 88.99	P-1	2
$BaLi_2P_2O_7$	7.078	12.164	13.856	Cmcm	8
$BaTi_2(P_2O_7)_2$	10.680 102.88	10.564	9.834	C2/c	4
$BaTi_2(P_2O_7)_2$	10.814 103.63	10. 64	9.821	C2/c	4
$BaTi_2(P_2O_7)_2$	10.621 103.71	10.468	9.706	C2/c	4

Characterization of $P_2O_7^{4-}$ in $BaMnP_2O_7$ by IR vibration spectrometry.

IR absorption spectra of various compounds are recorded in the interval 1500-350 cm^{-1} absorption field of the ions contained in condensed phosphates. As for the Raman scattering spectra, they are derived from 25 to 1500 cm^{-1}, including the field of external modes of cations and anions. Table 4 contains the main stretching and bending vibrations of $P_2O_7^{4-}$ anions [20].The IR absorption spectrum of $BaMnP_2O_7$ is reported in Fig 2 and the nature of the vibration corresponding to the different observed bands of $BaMnP_2O_7$ is given in Table 5.

Table 4:-IR Frequency characteristics (in cm^{-1}) for $P_2O_7^{4-}$ anions

Vibrations	**Frequencies**
ν_{as} (PO_3)	1115 – 1250 cm^{-1}
ν_s(PO_3)	1110 – 990 cm^{-1}
ν_{as}(POP)	960- 720 cm^{-1}
δ_{as} (PO_3)	660- 529 cm^{-1}
δ_s (PO_3)	529- 300 cm^{-1}



Wave number (cm^{-1})

Figure 2:-IR spectra of the phosphate $BaMnP_2O_7$

Table 5:-Frequencies (cm^{-1}) of IR absorption bands for $BaMnP_2O_7$

Frequencies (cm^{-1})	Vibrations
1116	ν_{as} (PO_3)
996	ν_s(PO_3)
920	ν_{as}(POP)
735	
572	δ_{as} (PO_3)
485	δ_s (PO_3)

$P_3O_{10}^{5-}$, $P_4O_{13}^{6-}$, $P_5O_{16}^{7-}$

Till now, there are no oligophosphates associated to barium for such anions.

Cyclophosphates $(P_nO_{3n})^{n-}$

$P_3O_9^{3-}$

$Ba_3\ (P_3O_9)_2{\cdot}4H_2O$

Chemical preparation of pure $Ba_3(P_3O_9)_2{\cdot}4H_2O$ is difficult to optimize. Large crystals of cyclotriphosphatetetrahydrate of barium, $Ba_3(P_3O_9)_2{\cdot}4H_2O$, were prepared by mixing 30 g of $BaCl_2{\cdot}2H_2O$ and 6 g of $Na_3P_3O_9$ (Ba/Na = 2) in 50 ml of water without stirring for 5 h, as shown in the following chemical reaction :

$$3BaCl_2{\cdot}2H_2O + 2Na_3P_3O_9 \longrightarrow Ba_3(P_3O_9)_2{\cdot}4H_2O + 6NaCl + 2H_2O.$$

$Ba_3(P_3O_9)_2{\cdot}4H_2O$ is stable until its melting point at 870°C.

$Ba_3(P_3O_9)_2{\cdot}6H_2O$

Chemical preparation of polycrystalline samples of the title compound, $Ba_3(P_3O_9)_2.6H_2O$ [21],were prepared by adding slowly dilute cyclotriphosphoric acid to an aqueous solution of barium carbonate, according to the following chemical reaction :

$$2H_3P_3O_9 + 3BaCO_3 \longrightarrow Ba_3(P_3O_9)_2.6H_2O + 3CO_2$$

The so-obtained solution was then slowly evaporated at room temperature until polycrystalline samples of $Ba_3(P_3O_9)_2.6H_2O$ were obtained. The cyclotriphosphoric acid used in this reaction was prepared from an aqueous solution of $Na_3P_3O_9$ passed through an ion-exchange resin "Amberlite IR 120"[9] [20].

$ZnBa_2(P_3O_9)_2.10H_2O$ and $MnBa_2(P_3O_9)_2.6H_2O$

Up to now there is only one cyclotriphosphate containing two divalent cations with a general formula $M^{II}M'^{II}2(P_3O_9)_2.nH_2O$. It's the cyclotriphosphatedecahydrate of barium and zinc, $ZnBa_2(P_3O_9)_2.10H_2O$, which was prepared by Durif et al. [22] using Boullé's process [23]. This salt is the only mixed-divalent cationcyclotriphosphate that has been reported in the chemical literature. So, the second example of such cyclotriphosphates is $MnBa_2(P_3O_9)_2.6H_2O$ [24-25]. This last cyclotriphosphate is isotypic of $Ba_3(P_3O_9)_2.6H_2O$ which was originally prepared through the use of Boullé's process [23] by Grenier and Martin [26] and its detailed structural characterization was later reported by Masse et al. [27].

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

$$2H_3P_3O_9 + 2BaCO_3 + MnCO_3 \longrightarrow MnBa_2(P_3O_9)_2.6H_2O + 3\ CO_2$$

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

$BaCsP_3O_9.2H_2O$

Single crystals of $BaCsP_3O_9.2H_2O$ [20,28], were prepared by slowlyadding dilute cyclotriphosphoric acid, $H_3P_3O_9$, to an aqueoussolution of barium carbonate, $BaCO_3$, and cesium carbonate, Cs_2CO_3, with a stoichiometric ratio Ba/Cs = 1, according to thefollowing chemical reaction:

$$H_3P_3O_9+BaCO_3+1/2Cs_2CO_3+1/2H_2O \longrightarrow BaCsP_3O_9.2H_2O + 3/2CO_2$$

$BaNH_4P_3O_9\cdot 2H_2O$

$BaNH_4P_3O_9\cdot 2H_2O$ was prepared from a new elaboration process [29]. Crystals of the title compound were prepared by adding slowly dilute cyclotriphosphoric acid to an aqueous solution of barium carbonate and ammonium carbonate with a stoichiometric ratio $Ba/NH_4=1$, according to the following chemical reaction:

$$H_3P_3O_9+ BaCO_3+1/2(NH_4)2CO_3 \rightarrow BaNH_4P_3O_9.2H_2O+3/2CO_2$$

The so-obtained solution is then slowly evaporated at room temperature until large rectangular prisms of $BaNH_4P_3O_9\cdot 2H_2O$ are obtained. The crystals are stable in air for many months under normal conditions of temperature and hygrometry.

$BaTlP_3O_9\cdot 2H_2O$

Single crystals of the title compound, $BaTlP_3O_9\cdot 2H_2O$ [29], were prepared by slowly adding dilute cyclotriphosphoric acid to an aqueous suspension of barium carbonate and thallium carbonate with a stoichiometric ratio Ba/Tl = ¼, according to the following chemical reaction:

$$H_3P_3O_9 + BaCO_3 + 1/2\ Tl_2CO_3+ 3/2\ H_2O \longrightarrow BaTlP_3O_9\cdot 2H_2O + 3/2\ CO_2$$

The so-obtained solution was then slowly evaporated at room temperature until large rectangular prisms of $BaTlP_3O_9\cdot 2H_2O$ were obtained. The crystals are stable in air for many months under normal conditions of temperature and hygrometry.

$BaTlP_3O_9$

Polycrystalline samples of $BaTlP_3O_9$ were prepared by total dehydration of $BaTlP_3O_9\cdot 2H_2O$ under atmospheric pressure between 300 and 500°C according to the following chemical reaction:

$$BaTlP_3O_9\cdot 2H_2O \longrightarrow BaTlP_3O_9 + 2H_2O$$

$BaTlP_3O_9$ was found to be stable until its melting point at 560°C [29].

$BaNaP_3O_9.3H_2O$

The title compound was obtained by adding $Ba(NO_3)_2.2H_2O$ to a saturated aqueous solution of $Na_3P_3O_9$ (15ml) in the stoichiometric ratio, according to the following chemical reaction:

$$Na_3P_3O_9+ Ba(NO_3)_2.H_2O \longrightarrow BaNaP_3O_9.3H_2O + 2NaNO_3+ H_2O$$

The resulting mixture was left to stand at room temperature for two weeks, after while pink crystals $BaNaP_3O_9.3H_2O$ appeared on the bottom of the beaker [30].

$BaNaP_3O_9\cdot 4H_2O$

The cyclotriphosphatetetrahydrate of barium and sodium $BaNaP_3O_9\cdot 4H_2O$ was first reported by Heitmann and Henneberg. Its chemical preparation and crystallographic data were reported by Martin and Durif [31], it’s isotypic with the corresponding silver-barium, **$BaAgP_3O_9.4H_2O$,** described below. The trihydrate was obtained by crystallization of an aqueous solution of the tetrahydrate at 60 °C. Averbuch-Pouchot and Durif [32] reported a complete description of its atomic arrangement.

$BaNaP_3O_9$

Barium trimetaphosphate was demonstrated in the study of the $Ba(PO_3)_2$-$NaPO_3$ system (Martin &Durif, 1972) [33].

$BaAgP_3O_9.4H_2O$

This hydrate, prepared by Boulle's process [23], was described by Durif and Averbuch-Pouchot[34] and its crystal structure was determined by Seethanen et al. [35].

$BaAgP_3O_9$

Crystal data for this salt, prepared by heating the corresponding tetrahydrate, described below, at 350 °C, were reported by Durif and Averbuch-Pouchot. [34] who identified it as an isotype of $BaNaP_3O_9$.

$BaKP_3O_9.H_2O$

This salt was first characterized by Martin. [36] and its atomic arrangement was subsequently determined by Seethanen and Durif [37].

$BaNa_4(P_3O_9)_2$

The main crystallographic features of $BaNa_4(P_3O_9)_2$ and its chemical preparation were reported by Averbuch-Pouchot and Durif [38] who identified this salt as an isotype of $PbNa_4(P_3O_9)_2$.

The crystallographic data for the cyclotriphosphates associated to bariumis given in Table 6.

Table 6:-Main Crystallographic Data for the cyclotriphosphates associated to barium

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	S.G.	Z
$Ba_3(P_3O_9)_2·4H_2O$	16.090	8.368 95.380	7.717	C2/m	2
$Ba_3(P_3O_9)_2.6H_2O$	7.547 108.58	11.975 100.35	13.068 95.54	P-1	2
$Ba_2Mn(P_3O_9)_2.6H_2O$	7.534 107.93	11.898 100.36	13.053 95.78	P-1	2
$Ba_2Zn(P_3O_9)_2.10H_2O$	26.52	7.625 100.93	12.92	C2/c	4
$BaNaP_3O_9.4H_2O$	21.33	7.01 122.18	18.26	C2/c	8
$BaAgP_3O_9.4H_2O$	21.35	7.163 121.72	18.35	C2/c	8
$BaNaP_3O_9.3H_2O$	7.0350 116.551	9.0470 95.932	9.88 74.088	P-1	2
$BaCsP_3O_9.2H_2O$	7.699	12.323 100.92	11.802	$P2_1/n$	4
$BaTlP_3O_9.2H_2O$	7.546	12.105 100.34	11.649	$P2_1/n$	4
$BaNH_4P_3O_9.2H_2O$	7.547	12.065 101.111	11.697	$P2_1/n$	4
$BaKP_3O_9.H_2O$	7.34	17.77 95.24	7.18	$P2_1/n$	4
$BaNa_4(P_3O_9)_2$	7.313 121.52	8.151 102.66	7.865 72.23	P-1	1

$BaTlP_3O_9$	11.086	12.283	5.786	$P2_12_12_1$	4
$BaNaP_3O_9$	11.055	12.278	5.785	$P2_12_12_1$	4

Characterization of $P_3O_9^{3-}$ in $Ba_3(P_3O_9)_2.6H_2O$by IR vibration spectrometry

The IR absorption spectrum of $Ba_3(P_3O_9)_2.6H_2O$ [21], is reported in (Fig 3). In the domain 4000-1600 cm^{-1}, the spectrum (Fig 3) shows two bands at 3416 and 1616 cm^{-1}. The band at 3416 cm^{-1} is attributed to the stretching vibrations of water molecules (ν OH). The band at 1616 cm^{-1} represents the bending vibration of water molecules (δ HOH). Between 1340 and 660 cm^{-1} , the spectrum (Fig 3) shows valency vibration bands characteristic of phosphates with ring anions $P_3O_9^{3-}$ [39]. Among these bands can be distinguished:

1. The vibration bands of the (OPO) end groups at high frequencies: $1180 < \nu_{as}$ OPO < 1340 cm^{-1} and $1060 < \nu_s$ OPO < 1180 cm^{-1};
2. the valency vibrations of the (P-O-P) ring groups at : $960 < \nu_{as}$ POP < 1060 cm^{-1} and $660 < \nu_s$ POP < 960 cm^{-1};

The valency vibrations of the (POP) ring groups are represented in the spectrum (Fig 3) by a very strong band at about 983 cm^{-1} which can be attributed to the ν_{as} POP antisymmetric vibrations and by a strong band between 700 and 800 cm^{-1} (at 744 cm^{-1}) which can be related to the ν_s POP symmetric vibrations. The strong band at 744 cm^{-1} characterize with no ambiguity the structure of a cyclotriphosphate $P_3O_9^{3-}$. Between 660 and 400 cm^{-1} the spectrum (Fig 3) shows bending vibration bands characteristic of phosphates with ring anions. The nature of the vibration corresponding to the different observed bands is given in Table 7.

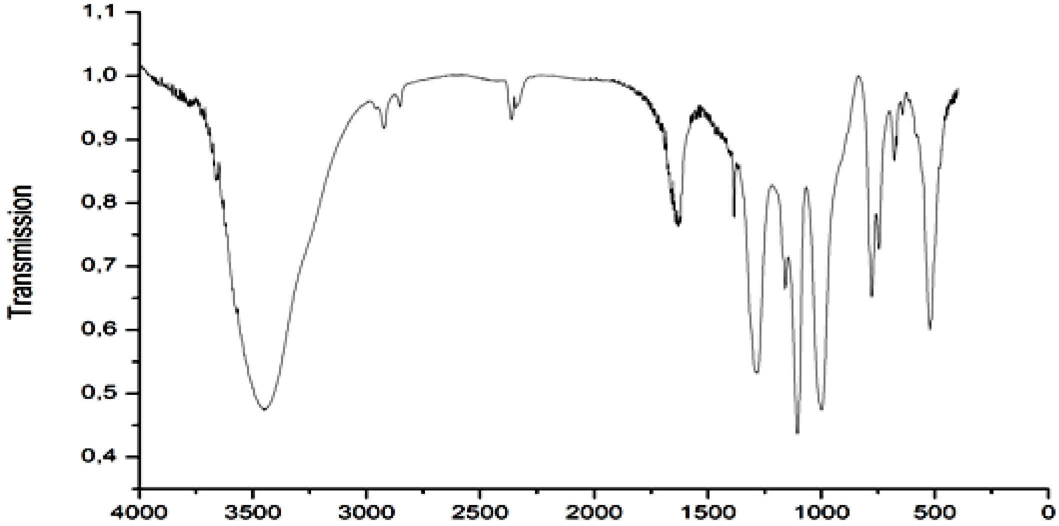


Figure 3:-IR spectra of the phosphate $Ba_3(P_3O_9)_2.6H_2O$

Table 7:-Frequencies (cm^{-1}) of IR absorption bands for $Ba_3(P_3O_9)_2.6H_2O$

Frequencies (cm^{-1})	Vibrations
3416	ν OH
1616	δ HOH
1307	ν_{as} OPO
1271	
	ν_s OPO
1159	
1120	
1103	
	ν_{as} POP
983	
871	
	ν_s POP
744	
688	
	δ OPO
645	+
635	ρ OPO
526	

$P_4O_{12}^{4-}$ $Ba_2P_4O_{12}{\cdot}4H_2O$.

This hydrate was characterized by Nariai et al. [40]. The investigation, both in a dry and in a humid atmosphere, of its thermal behavior shows that crystallization water is released at about 150 °C. At 510 °C, the long-chain polyphosphate is observed after an intermediate step corresponding to an amorphous phase containing mainly oligophosphates. No crystal data exist for this compound.

Characterization of $P_4O_{12}^{4-}$ by IR vibration spectrometry

Foumakoye et al. [41] studied by IR absorption spectroscopy and Raman scattering, many cyclotetraphosphates with structures determined by X-ray diffraction and adopted the same approach as that of K. Sbai [42] for a cycle of order 3. The IR absorption spectrum of $Ba_2P_4O_{12}{\cdot}4H_2O$ is reported in Fig 4.

The detailed examination of the IR spectra of a series of cyclotetraphosphates of different symmetries : S_4, C_{2v}, C_i, C_{2h} and C_1, allowed Foumakoye et al. [41] to identify a general pattern characterized by five distinct areas namely :

¬ from 1330 to 1180 cm^{-1}: antisymmetric vibrations ν_{as} OPO-.
¬from 1180 to 1080 cm^{-1}: symmetrical vibrations ν_s OPO-.
¬ 1060-960 cm^{-1}: antisymmetric vibrations δ_{as} POP.
¬ 850-660 cm^{-1}: symmetrical vibrations δ_s POP.
¬ 660-500 cm^{-1}: cycle bending, translations and rotations.

The nature of the vibration corresponding to the different observed bands is given in Table 8.

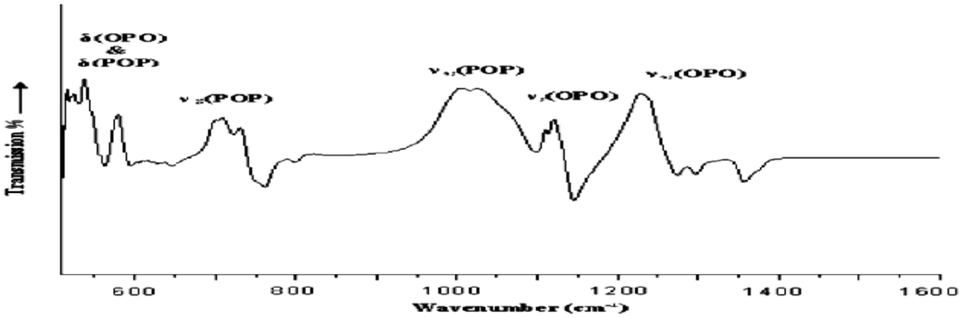


Figure 4:-IR spectra of the phosphate $Ba_2P_4O_{12}{\cdot}4H_2O$

Table 8:-Frequencies (cm^{-1}) of IR absorption bands for $Ba_2P_4O_{12}\cdot4H_2O$

Frequencies (cm^{-1})	Vibrations
1328 1281	ν_{as} OPO$^-$
1224 1136	ν_s OPO$^-$
1120	ν_{as} POP
1087 803 733	ν_s POP
581 539 527	δ POP + δ OPO$^-$

$P_6O_{18}^{6-}$ $Ba_3P_6O_{18}\cdot9H_2O$ and $Ba_3P_6O_{18}\cdot8H_2O$.

Thilo and Schülke [43] and Lazarevski and al. [44] obtained $Ba_3P_6O_{18}\cdot9H_2O$ as a white crystalline substance from the reaction between aqueous solution of $BaCl_2$ and $Na_6P_6O_{18}$. Recently, Rzaigui et al. [45] described the chemical preparation of the octahydrate and determined its crystal structure.

$Ba_3P_6O_{18}\cdot8H_2O$ crystallizes in the monoclinic system C2/c and the unit-cell parameters, a = 2098(2) Å, b = 7.227(3) Å, c = 17.44 (3) Å; Z = 4 and β= 119.56 (5).

Characterization of $P_6O_{18}^{6-}$ in $Ba_3P_6O_{18}.8H_2O$ by IR vibration spectrometry

The IR absorption spectrum of $Ba_3P_6O_{18}.8H_2O$ is reported in (Fig 5).The most outstanding features noted in the IR spectra of cyclohexaphosphates were specified by G. Foumakoy and al. [41] and K. Sbai [42].

¬ Between 1300 and 1210 cm^{-1}: antisymmetric vibration ν_{as} OPO$^-$.
¬ Between 1200 and1110 cm^{-1}: symmetric vibration ν_s OPO$^-$.
¬ Between 1100 and 940 cm^{-1}: antisymmetric vibration ν_{as} POP.
¬ Between 890 and 650 cm^{-1}: symmetric vibrations ν_s POP.
¬ Between 640 and 500 cm^{-1}: angular deformation vibrations δ OPO-
¬ Between 450 and 300 cm^{-1}: angular deformation vibrations δ POP

The nature of the vibration corresponding to the different observed bands is given in Table 9.

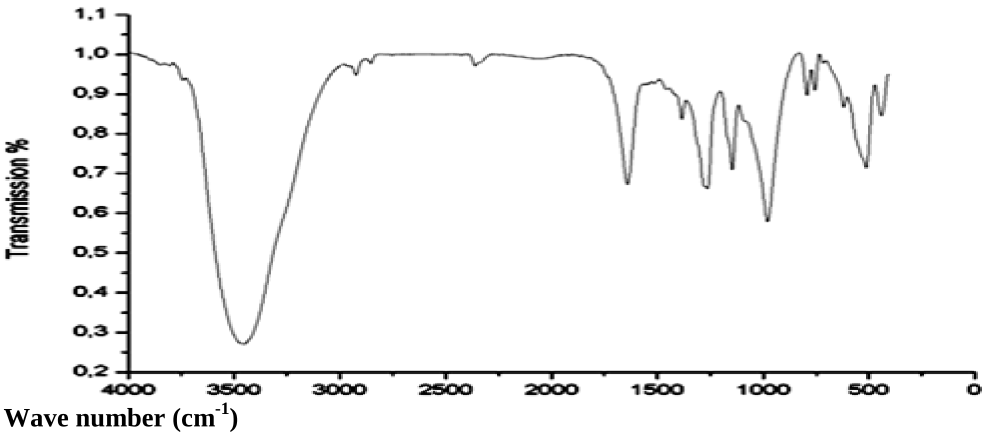


Figure 5:-IR spectra of the phosphate $Ba_3P_6O_{18}.8H_2O$

Table 9: Frequencies (cm^{-1}) of IR absorption bands for $Ba_3P_6O_{18}.8H_2O$

Frequencies (cm^{-1})	Vibrations
3453	ν (O-H)
1637	δ (H-O-H)
1381	ν_{as} OPO^-
1273	
1142	ν_s OPO^-
980	ν_{as} POP
795	
751	ν_s POP
512	δ OPO^-
436	δ POP

$P_{10}O_{30}^{10-}$ $Ba_2Zn_3P_{10}O_{30}$

The preparation of single crystals of $Ba_2Zn_3P_{10}O_{30}$ by the use of a flux method was first reported by Bagieu-Beucher et al. [46]. These authors dissolved $BaCO_3$ and $ZnCO_3$ in stoichiometric amounts in an excess of H_3PO_4 and heated the mixture for several days at 400 °C. Polycrystalline samples were obtained by heating a stoichiometric mixture of $BaCO_3$, $ZnCO_3$, and $(NH_4)_2HPO_4$ for several days at 600-650 °C. Recently, Schülke [47] considerably improved these procedures. When a mixture of $BaCO_3$, $ZnCO_3$, and H_3PO_4 in the stoichiometric ratio was seeded with a few crystals of $Ba_2Zn_3P_{10}O_{30}$ and heated at 500 °C in a platinum crucible for 2h, $Ba_2Zn_3P_{10}O_{30}$ was obtained in 100% yield. Crystals used as seeds in this procedure are prepared by melting a stoichiometric mixture of $BaCO_3$, $ZnCO_3$, and H_3PO_4 at 750 °C for 10 min. The melt is then tempered at 400 °C for 12 h. This procedure is sometimes unsuccessful and leads to a mixture of various condensed phosphates.

$Ba_2Zn_3P_{10}O_{30}$ crystallizes in the monoclinic system P2/n and the unit-cell parameters, a = 21.738(1) Å, b = 5.356(2) Å, c = 10.748 (4) Å; Z = 2 and β= 99.65 (3).

Characterization of $P_3O_{10}^{5-}$by IR vibration spectrometry

Till now there is no triphosphate, P_3O_{10},combined with barium cation. But we can afford for lecturers a detailed description for the calculated IR frequencies for the $P_3O_{10}^{5-}$ anions and the movements for each vibration.

The $P_3O_{10}^{5-}$ anion was studied in the range 4000 – 400 cm^{-1}. Band assignments for the fundamental modes, of valence and bending, of $P_3O_{10}^{5-}$ anions are presented in Table 10. The frequencies of the $P_3O_{10}^{5-}$ anion are assigned on the basis of the characteristic vibrations of the P–O–P Bridge, PO_2 and PO_3 groups. As the P–O bond in the PO_2 and PO_3 group is weaker than that in the P–O–P Bridge, the vibrational frequencies of PO_2 and PO_3 are expected to be higher than those for P–O–P. The bands due to the symmetric and antisymmetric stretching frequencies of PO_2 and PO_3 in $P_3O_{10}^{5-}$ are generally observed in the region 1190–1010 cm^{-1}[48]. The bands observed in the domain 970–840 cm^{-1} are attributed to the antisymmetric and symmetric POP stretching modes. The bands due to δ(OPO), δ(PO_2), δ(PO_3) and δ(POP) are also identified in Table 10.

Table 10:-Calculated IR Frequencies of the $P_3O_{10}^{5-}$ anions by IR vibration spectrometry

Calculated IR frequencies (cm^{-1})	Vibrations
1319	νP=O
1253	ν_{as} PO_2
1249	
1245	
1170	ν_{aa} PO_3
1081	ν_s PO_2
1059	$\nu_a PO_3$
962	
891	ν_{as} POP
724	

671	ν_s POP
605	δPO_2
560	δPO_3

I$P_5O_{15}^{5-}$, $P_8O_{24}^{8-}$, $P_{12}O_{36}^{12-}$

Till now, there are no cyclophosphates associated to barium for such anions.

Long chain polyphosphates $(PO_3^-)_n$

β-$Ba(PO_3)_2$ and γ-$Ba(PO_3)_2$

Thilo and Grunze[49] identified $Ba(PO_3)_2$ during the study of the thermal dehydration of $Ba(H_2PO_4)_2$. This polyphosphate is polymorphic. Grenier and Martin [50], reported the existence of three forms of $Ba(PO_3)_2$. The normal *β* form already described, a high-temperature form called *α* and a third form (γ) accidentally produced during their investigations. According to these authors.

$$\gamma\text{-}Ba(PO_3)_2 \xrightarrow{978\ K} \beta\text{-}Ba(PO_3)_2$$

$$\beta\text{-}Ba(PO_3)_2 \xrightarrow{1058\ K} \alpha\text{-}Ba(PO_3)_2$$

$BaMn(PO_3)_4$, $BaCd(PO_3)_4$, $BaCa(PO_3)_4$ and $BaHg(PO_3)_4$.

The $Ba(PO_3)_2$-$Cd(PO_3)_2$ and $Ba(PO_3)_2$-$Ca(PO_3)_2$ phase equilibrium diagrams were elaborated by Bukhalova et al. [51]. $BaCd(PO_3)_4$ and $BaCa(PO_3)_4$, both congruent-melting long-chain polyphosphates (815 °C for Cd and 880 °C for Ca), were observed in these systems. The existence of these two isotypic salts was confirmed by Averbuch-Pouchot[52] who reported their main crystallographic features as well as those of two other isotypic compounds, $BaMn(PO_3)_4$ and $BaHg(PO_3)_4$. The atomic arrangement of this series of compounds was determined by Averbuch-Pouchot et al. [53] using the cadmium salt. An IR spectroscopic investigation of $BaCa(PO_3)_4$ and $BaCd(PO_3)_4$ was reported by Tokman and Poletaev[54].

$Ba_2K(PO_3)_5$.

Crystals of $Ba_2K(PO_3)_5$ wereobtained by heating at 480°C for 24 hours 1 gram of barium carbonate, 5 grams of potassium carbonate and 10 cm^3 of orthophosphoric acid 85%. The crystals obtained are thick platelet hexagonal contours [55].

$Ba_2Cs(PO_3)_5$.

Itsatomic arrangement was determined by Masse and Averbuch-Pouchot [56]. $Ba_2Cs(PO_3)_5$ is an incongruent melting compound decomposing at 720 °C. The crystal data reported by the authors showed this polyphosphate to be isotypic with $Ba_2K(PO_3)_5$

$Ba_2NH_4(PO_3)_5$

$Ba_2NH_4(PO_3)_5$is isostructural with $Ba_2K(PO_3)_5$ and $Ba_2Cs(PO_3)_5$ [57]. The optimal conditions for preparation of the compound are 300°C and the molar ratio BaO: NH_4PO_3 = 1:3. An increase of temperature and reaction time causes the step-by-step crystallization of the following compounds in the system:

$Ba(NH_4)_4(PO_3)_6 \rightarrow Ba_2NH_4(PO_3)_5 \rightarrow Ba(PO_3)_2$.

$Ba(NH_4)_4(PO_3)_6$

A mixture of BaO and NH_4PO_3 in the molar ratio 1:8 was placed in a wide silica crucible and kept under atmospheric conditions at 300 °C in a laboratory furnance[58].

$BaCs_4(PO_3)_6$

The final product of total thermal dehydration of $BaCsP_3O_9.2H_2O$, between 500 and 600°C is the long chain polyphosphate of barium and cesium $BaCs_4(PO_3)_6$ [28].

$Ba_2Cu(PO_3)_6$ and $Ba_2Zn(PO_3)_6$

$Pb(PO_3)_2$-$Cu_2P_4O_{12}$, $Sr(PO_3)_2$-$Cu_2P_4O_{12}$ and $Ba(PO_3)$-$Cu_2P_4O_{12}$ phase-equilibrium diagrams were elaborated by Laiigt[59]. The first two diagrams are of the eutectic type 650 °C, 20% $Pb(PO_3)_2$ and 780 °C, 40% $Sr(PO_3)_2$], but the third one shows the existence of $Ba_2Cu(PO_3)_6$, a congruent melting (830°C) long-chain polyphosphate. The atomic arrangement of $Ba_2Cu(PO_3)_6$ was later determined by Laiigt[59].

$Ba_2Li_3(PO_3)_7$

Owing to a lack of accuracy in the determination of the $LiPO_3$-$Ba(PO_3)_2$ phase-equilibrium diagram by Martin [36], the only compound reported in this study was originally thought to correspond to $BaLi(PO_3)_3$. A re-examination of this diagram by El-Horr[60] showed that the correct formula is $Ba_2Li_3(PO_3)_7$. The crystal structure determination performed by N. El-Horr et al. [61] confirmed this formula.

Table 11:-Main Crystallographic Data for the polyphosphates associated to barium

Formula	a(Å) α°	b(Å) β°	c(Å) γ°	S.G.	Z
β-$Ba(PO_3)_2$	4,51	13,44	8.360	$P2_12_12_1$	4
γ-$Ba(PO_3)_2$	9.692	6.894 94.77	7.512	$P2_1/n$	4
$BaMn(PO_3)_4$	14.69	9.147 90.57	7.201	$P2_1/n$	4
$BaCd(PO_3)_4$	14.94	9.192 90.79	7.219	$P2_1/n$	4
$BaCa(PO_3)_4$	15.24	9.173 90.96	7.231	$P2_1/n$	4
$BaHg(PO_3)_4$	15.05	9.236 90.62	7.239	$P2_1/n$	4
$Ba_2K(PO_3)_5$	8.646	7.329 129.17	13.884	Pc	2
$Ba_2Cs(PO_3)_5$	8.444	7.509 125.31	13.976	Pc	2
$Ba_2NH_4(PO_3)_5$	8.649	7.312 128.14	13.873	Pc	2
$Ba(NH_4)_4(PO_3)_6$	11.1911	11.1911	8.9375	$P3_1c$	2
$BaCs_4(PO_3)_6$	11.541	11.541	9.112	$P3_1c$	2
$Ba_2Cu(PO_3)_6$	21.382	7.286 97.96	9.520	$P2_1/a$	4
$Ba_2Zn(PO_3)_6$	21.52	7.278 97.83	9.534	$P2_1/a$	4
$Ba_2Li_3(PO_3)_7$	18.0148	8.535	11.584	$P2_1/a$	4
		104.48			

Characterization of PO_3^-in β [$Ba(PO_3)_2$]by IR vibration spectrometry

Characterization of β [$Ba(PO_3)_2$] by IR vibration spectrometry. The IR absorption spectrum of β [$Ba(PO_3)_2$] is reported in Fig 6. Between 1300 and 650 cm^{-1} the spectrum Fig 6, shows valency vibration bands characteristic of long-chain polyphosphates PO_3^-. Among these bands can be distinguished:

1. The vibration bands of the (OPO) end groups at high frequencies: $1200 < \nu_{as}$ OPO $< 1300\ cm^{-1}$ and $1100 < \nu_s$ OPO $< 1170\ cm^{-1}$;
2. The valency vibrations of the (P-O-P) chain groups at: $850 < \nu_{as}$ POP $< 1050\ cm^{-1}$ and $650 < \nu_s$ POP $< 800\ cm^{-1}$;

The valency vibrations of the (POP) chain groups are represented in the spectrum Fig 6, by a strong band at about 865 cm^{-1} which can be attributed to the ν_{as} POP antisymmetric vibrations. This strong band which is situated generally between 850 cm^{-1} and 940 cm^{-1} (in this case at 865 cm^{-1}) characterize with no ambiguity the structure of a long-chain polyphosphate PO_3^- . The strong band which is situated at 865 cm^{-1} and corresponding to the ν_{as} POP antisymmetric vibration, characterize with no ambiguity the structure of a long-chain polyphosphate PO_3^- . By the examination of the position, the profile and the intensity of this band which doesn't appear in the IR spectra of the cyclotriphosphates $P_3O_9^{3-}$ and which is located generally between 850 cm^{-1} and 940 cm^{-1}, it is then possible to distinguish between cyclotriphosphate $P_3O_9^{3-}$ and long-chain polyphosphate PO_3^-. Between 600 and 400 cm^{-1} the spectrum Fig 3, shows bending vibration bands characteristic of long-chain polyphosphates. The nature of the vibration corresponding to the different observed bands is given in Table 12.

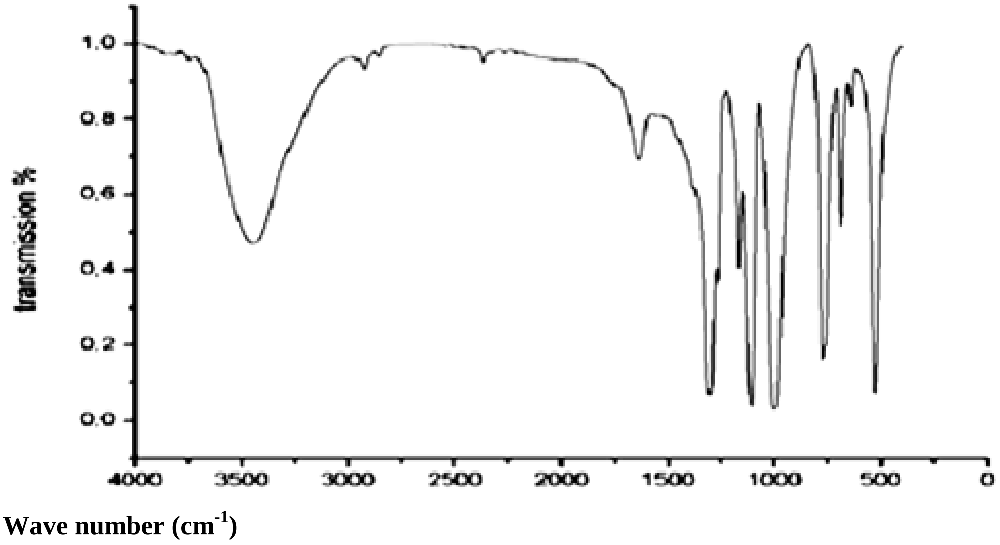


Figure 6:-IR spectra of the phosphate β-Ba(PO$_3$

Table 12: Frequencies (cm^{-1}) of IR absorption bands for β-$Ba(PO_3)_2$

Frequencies (cm^{-1})	Vibrations
1305	
1158	ν_{as} OPO^-
1086	ν_{as} OPO^-
1023	ν_{as} POP
865	
772	ν_s POP
686	
636	δ OPO^- + ρ OPO^-
563	
510	
431	

Ultraphosphates $[P_{(2+n)}O_{(5+3n)}]^{n-}$

Till now, there are no cyclophosphates associated to barium for such anions.

Conclusion:-

We have collected crystallographic data for condensed phosphates and monophosphates associated to barium with known structures. Various condensed phosphates and monophosphates, especially there anions, were characterized by infrared vibration spectrometry. Different methods of preparations of condensed phosphates were cited here (Boulle's process, classical methods, thermal methods as dehydration, flux methods, ion-exchange resins and non-conventional methods). Till now there are no condensed phosphates with the following anions: cyclophosphates

$P_nO_{3n}^{n-}$ (3 type of anions :$P_5O_{15}^{5-}$, $P_8O_{24}^{8-}$, $P_{12}O_{36}^{12-}$) and oligophosphates $(P_nO_{3n+1})^{(n+2)-}$ (3 type of anions : $P_3O_{10}^{5-}$, $P_4O_{13}^{6-}$, $P_5O_{16}^{7-}$). In no way we have extrapolated these ideas to design possible but not yet existing compounds. It is certainly a pleasant game for rainy days to play with the infinite possibilities of tetrahedron linkage geometry, but it remains a game. For instance, it is rather evident that branched polyphosphates or cyclophosphates will one day be characterized. We understand perfectly well that such ideas may become the objects of controversies but we just want to open a field of discussions among the scientists involved in the more and more complex problems of phosphate chemistry.

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