

Layered Crystalline Barium Phenylphosphonate as Host Support for *n*-Alkylmonoamine Intercalation

ANGÉLICA M. LAZARIN and CLAUDIO AIROLDI*

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13084-971 Campinas, São Paulo, Brazil

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Abstract

Layered barium phosphonate, synthesized by combining the metallic salt with a phenylphosphonic acid solution, yielded $\text{Ba}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$ (BaPP), which gives the corresponding anhydrous compound on heating. *n*-Alkylmonoamines intercalation into the crystalline lamellar precursor resulted in compounds having the general formula $\text{Ba}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot x\text{H}_2\text{N}(\text{CH}_2)_n\text{CH}_3 \cdot (1-x)\text{H}_2\text{O}$ ($n = 1-5$). The intense infrared bands in the $1160-695 \text{ cm}^{-1}$ interval confirmed the presence of the phosphonate groups attached to the inorganic layer, with sharp and intense peaks in X-ray diffraction patterns for both hydrated and anhydrous compounds. The thermogravimetric curves for both supports showed the release of water molecules and the organic moiety in distinct stages to yield a final $\text{Ba}(\text{PO}_3)_2$ residue. An additional amine mass loss steps was observed for the corresponding aminated compounds. One isolated DSC peak found in the layered precursor compound contrasts by its absence in the anhydrous form and the ^{31}P NMR spectrum presented one peak for attached phenylphosphonate groups centered at 12.4 ppm. An increase in carbon and hydrogen percentages for intercalated compounds followed the amine size chain with a corresponding decrease in nitrogen percentage. The interlayer distance (d) correlates linearly with the number of carbon atoms (n_c) of the alkylamine chains, $d = 1467 + 62n_c$ and $d = 1688 + 60n_c$, for the hydrated and anhydrous compounds, respectively, permitting inference of the interlayer distance for an unknown amine.

Introduction

Layered crystalline metal phosphonate compounds have attracted a great deal of research activity as expressed in a recent review [1–3]. The potential applications of such compounds manifested as ion-exchangers, sorbents, sensors, proton conductors, nonlinear optical materials, active photochemical materials, catalysts, and hosts for intercalation of a variety of guest molecules [4–9]. The layered metal phosphonate is also easily pillared to yield new materials, whose arrangement is prone to incorporate specific and selective species with a wide variety of properties, which can be available for a series of convenient applications [4, 10–14].

The majority of organophosphonate compound preparation methods is based on direct reaction of a metallic salt in aqueous solution, in the presence of the desired alkyl- or arylphosphonic acids [1, 7, 15–17]. The first derivatives were focused on tetravalent metals, as was previously applied to phosphates. The $\alpha\text{-Zr}(\text{C}_6\text{H}_5\text{PO}_3)_2$ structure determination was first studied through the powder diffraction method [18]. The

layered structure of these compounds is built up through oxygen-bridged metal octahedra, which are separated by the hydrophobic regions of the organic moieties and the phosphonate groups lie above and below the metal atom planes [19].

Nearly a decade after the zirconium phosphonate preparation, a series of similar divalent compounds, with the general formula $\text{M}(\text{O}_3\text{PR}) \cdot \text{H}_2\text{O}$ was also synthesized. The majority of them have six coordinated metal atoms [4] and some layered alkaline earth organophosphonates, such as magnesium [20], calcium [21–23] and barium [24] were also reported.

Presently, a large variety of organic groups have been placed inside the free space cavity, with or without active moieties, in an attempt to develop new materials. Efforts by academic or technological research interests have been encouraged by the recent discovery of porous structures in metal phosphonate compounds, which has caused an intense search for new materials [25, 26].

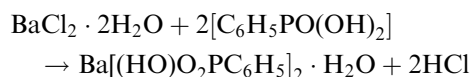
The aim of this publication is to explore the syntheses and characterization of the compound $\text{Ba}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$, its anhydrous derivative, and the products from intercalation of *n*-alkyl monoamines of the general formula $\text{CH}_3(\text{CH}_2)_n\text{NH}_2$ ($n = 1-5$).

* Author for correspondence. E-mail: airoldi@iqm.unicamp.br

Experimental

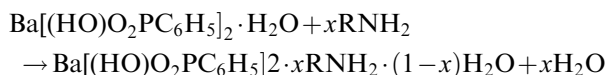
Preparation of barium phenylphosphonate (BaPP)

Hydrated barium phenylphosphonate was prepared by reacting 60.0 cm³ of a 1.0 mol dm⁻³ aqueous solution of phenylphosphonic acid (Aldrich) with 25.0 cm³ of 0.50 mol dm⁻³ of BaCl₂ · 2H₂O (Merck). To this mixture, maintained with vigorous stirring, 1.0 mol dm⁻³ of NaOH (Vetec) solution was added drop wise to adjust to a pH of 5–6. An abundant white solid immediately settled. The compound BaPP was isolated by filtration, washed with doubly distilled water and air dried at 320 K. This compound was dehydrated by heating the sample at 573 K in vacuum for 8 h to yield the anhydrous compound (BaPP1). The general synthetic reaction can be written as:



Intercalation

The intercalation was carried out by suspending about 50.0 mg of solid BaPP or BaPP1 in 0.50 mol dm⁻³ solutions of each amine dissolved in ethanol or 1,2-dichloroethane at room temperature, respectively. The isotherms of concentration vs. time were obtained through the batch method [26–33]. For this determination, a series of flasks containing the suspension was continuously stirred in a mechanical orbital apparatus thermostated at 298 ± 1 K. The interactive process at the solid liquid interface involving all *n*-alkyl monoamines RNH₂ can be generally represented as follows:



The number of moles of amine intercalated into the host matrix (n_f) can be calculated [30, 34, 35] by the difference between the initial number of moles (n_i) of added amine, and that determined in the supernatant (n_s), divided by the mass (m) of the compound used, as illustrated by the expression $n_f = (n_i - n_s)/m$. All amine solutions were previously standardized with 0.1570 mol dm⁻³ of hydrochloric acid solution, using as indicator 5:1 mixture of bromocresol green and methyl red [30]. After intercalation, this resulting white solid was separated by centrifugation and dried at 323 K in an oven for about 8 h. The isotherms presented an increase in number of moles of amines intercalated (n_f) with time (t) or with the concentration of the supernatant (C_s). In all cases, these intercalation processes caused a total saturation of the inorganic layered structure to establish a well-defined plateau.

Characterization of the materials

Barium [24] and phosphorus [36, 37] elemental analyses were determined through atomic absorption spectroscopy using a Perkin–Elmer Model 5100 atomic absorption spectrometer and spectrophotometric methods using a Shimadzu Model MultiSpec-1501 spectrophotometer, respectively. Carbon, hydrogen and nitrogen were obtained using a Perkin–Elmer model PE 2400 instrument for the precursor and intercalated compounds.

X-ray diffraction patterns were obtained with nickel-filtered CuK α radiation on a Shimadzu XD3-A diffractometer (30/20 kV/mA).

Infrared spectra were performed in a Perkin–Elmer model 1600 FTIR spectrophotometer by using pressed KBr pellets, with 4 cm⁻¹ of resolution.

Thermogravimetric curves were recorded using a DuPont model 1090 B apparatus coupled to a model 951 thermobalance by heating samples from room temperature to 1273 K at a heating rate of 0.16 K s⁻¹ in an argon flow of 1.67 cm³ s⁻¹. The samples varied in weight from 15.0 to 30.0 mg. Differential scanning calorimetry was carried out on a Shimadzu instrument, model DSC-50, using the same thermogravimetric conditions, but with a temperature interval from 298 to 873 K, with samples varying in weight from 3.0 to 5.0 mg.

The surface area measurements were performed on a Micromeritics Flow-Sorb 2300 instrument through gaseous nitrogen adsorption at 77 K, by applying the BET method.

The scanning electron microscopic (SEM) images were obtained for samples dispersed on a double-faced conducting tape adhered to an aluminum support. The samples were coated with gold using a low voltage sputtering Balzer MED 020 apparatus, and the measurements were carried out on a JEOL JSM-T300 scanning electron microscope.

The nuclear magnetic resonance spectra of the solid material were obtained on an AC 300/P Bruker spectrometer at room temperature at 121.0 and 75.5 MHz for phosphorus and carbon, respectively. A pulse repetition time of 3 s and contact time of 3 ms were used.

Results and discussion

The elemental analyses of in carbon, hydrogen and nitrogen in the layered crystalline hosts and their corresponding intercalated compounds were performed, as listed in Table 1. In addition, barium and phosphorus were also determined for the precursor hosts to give 28.2 and 12.7% for hydrated BaPP and 30.5 and 13.7% for anhydrous BaPP1 compounds, respectively. By comparing these results with the required amounts 28.2, 12.7, 29.5, 3.0 and 30.5, 13.7, 31.9, 2.7% for barium, phosphorus, carbon and hydrogen elements, respectively, with good agreement for chemical formulas

Table 1. Percentages of carbon (C), hydrogen (H) and nitrogen (N) for hydrated (BaPP) and anhydrous (BaPPI) barium phenylphosphonates and intercalated *n*-alkylmonamine compounds

Compound	C (%)	H (%)	N (%)
BaPP	29.5	3.0	–
BaPP · <i>x</i> CH ₃ CH ₂ NH ₂ · (1- <i>x</i>)H ₂ O	33.7	4.8	2.9
BaPP · <i>x</i> CH ₃ (CH ₂) ₂ NH ₂ · (1- <i>x</i>)H ₂ O	33.9	5.0	2.6
BaPP · <i>x</i> CH ₃ (CH ₂) ₃ NH ₂ · (1- <i>x</i>)H ₂ O	34.1	5.1	2.4
BaPP · <i>x</i> CH ₃ (CH ₂) ₄ NH ₂ · (1- <i>x</i>)H ₂ O	34.2	5.3	2.3
BaPP · <i>x</i> CH ₃ (CH ₂) ₅ NH ₂ · (1- <i>x</i>)H ₂ O	34.4	5.4	1.7
BaPPI	31.9	2.7	–
BaPPI · CH ₃ CH ₂ NH ₂	34.7	4.4	3.1
BaPPI · CH ₃ (CH ₂) ₂ NH ₂	35.0	4.7	2.8
BaPPI · CH ₃ (CH ₂) ₃ NH ₂	35.3	4.9	2.6
BaPPI · CH ₃ (CH ₂) ₄ NH ₂	35.6	5.1	2.5
BaPPI · CH ₃ (CH ₂) ₅ NH ₂	35.9	5.5	2.0

Ba(HO₃)PC₆H₅)₂·H₂O and Ba(HO₃)PC₆H₅)₂ for these hosts.

The high degree of crystallinity of the Ba(HO₃)PC₆H₅)₂·H₂O compound reflects in well-formed X-ray diffraction powder patterns, showing the presence of a sharp and intense peak attributed to the 001 plane, with an interlayer spacing plane at 5.8°, to give an interlayer distance of 1532 pm, as seen in Figure 1a. The corresponding anhydrous compound displayed its principal intense peak at 4.9°, as shown in Figure 1b, which gives an interlayer distance of 1751 pm. This increase in distance caused by water removal was interpreted as a distortion of the original structure, as observed for similar organophosphonate compounds [16].

A series of infrared spectra covering the hydrated, anhydrous and intercalated forms with alkylmonoamines are shown in Figure 2. For all infrared spectra a weak and broad band appeared at 3500 cm⁻¹ due to the OH groups that contrasts with its absence in the anhydrous form. The carbon–hydrogen and carbon–carbon stretching vibrations of the phenyl ring are present near 3000 cm⁻¹ as weak bands and at 1400 cm⁻¹ as a weak and well defined band, respectively. The bands around 2750 and 2340 cm⁻¹ are characteristics for O–H stretching frequencies of monohydrogen phosphonate groups. Intense phosphorus–carbon stretching vibrations appeared around 1600 cm⁻¹, and strong bands attributed to phosphorus–carbon stretching vibrations for the carbon-phosphate tetrahedral group are observed near 1000 cm⁻¹. Connected to this band, the out-of-plane monosubstituted phenyl ring vibrations appeared at 695 and 750 cm⁻¹, respectively [24]. The infrared spectra of the amine intercalation compound are very similar to the original layered host compounds.

The thermogravimetric (TG) curves for hydrated and anhydrous barium compounds and those obtained by intercalation with ethylamine are shown in Figure 3. The hydrated compound presented a mass loss of 4.0% from 560 to 610 K, with corresponds to the calculated weight mass loss of one water molecule. The release of the

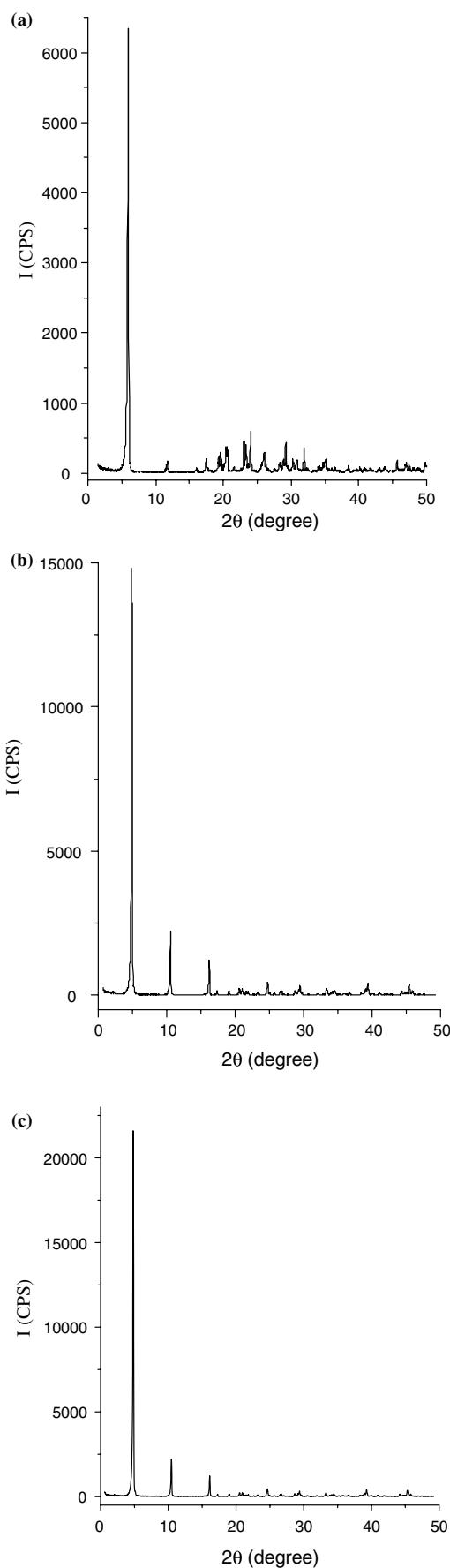


Figure 1. X-ray diffraction patterns of hydrated barium phenyl phosphonate (a), anhydrous barium phenylphosphonates (b) and hydrated compound intercalated with ethylamine (c).

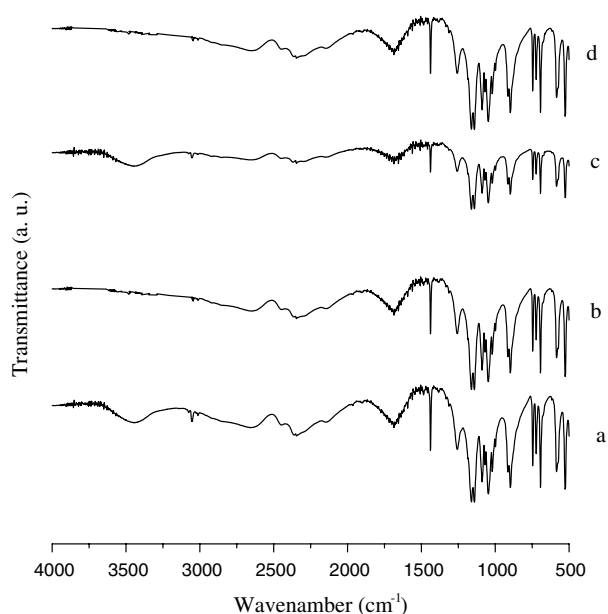


Figure 2. Infrared spectra of hydrated barium phenylphosphonate (a), anhydrous barium phenylphosphonates (b), hydrated compound intercalated with ethylamine (c) and anhydrous compound intercalated with ethylamine (d).

organic groups started around 720 K for both compounds and is completed at 920 K, but, in this stage some residual carbon is proposed, as previously reported [24]. The observed mass loss of 32.12% corresponding to the organic moiety is in agreement with a calculated value of 34.1%. The total mass loss of 35.0% up to 1270 K is consistent with the expected value of 34.6%, calculated for the conversion of $\text{Ba}(\text{HO}_3)\text{PC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$ to the final

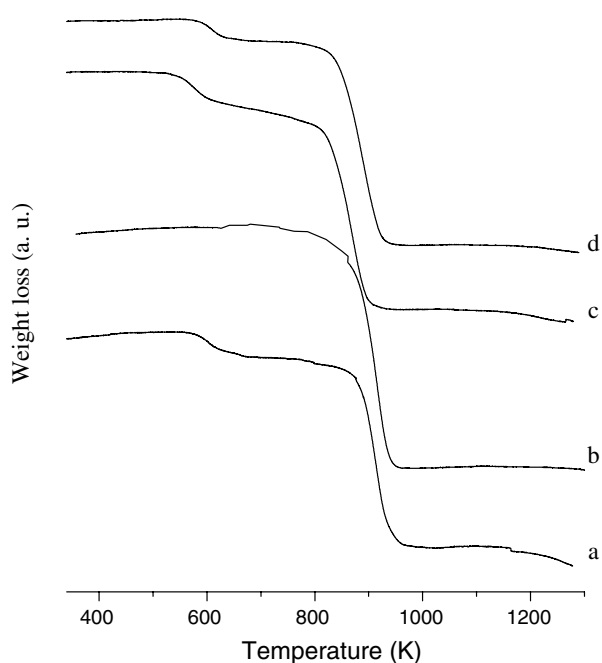


Figure 3. Thermogravimetric curves of hydrated barium phenylphosphonate (a), anhydrous barium phenylphosphonates (b), hydrated compound intercalated with ethylamine (c) and anhydrous compound intercalated with ethylamine (d).

$\text{Ba}(\text{PO}_3)_2$ residue [24]. The anhydrous TG curves for the compound, shown in Figure 3b, illustrate the absence of mass loss up to 560 K. This relevant feature emphasizes the difference between both host compounds, confirming the anhydrous form, obtained from the original hydrated compound, upon which continued heating gave the same final product $\text{Ba}(\text{PO}_3)_2$. The curves for the intercalated compounds are very similar to those observed for the precursor hydrated crystalline compounds with a difference in percentages at the decomposition stage. As discussed previously, water elimination caused a mass loss of 4.0%, while for the amine derivatives this percentage is always larger, varying from 5.4 to 7.7%. On examining these intercalated compounds the following processes were detected: (i) physically-adsorbed amine and water molecule are lost from room temperature to near 560 K; (ii) the chemisorbed amine is lost from 560 up to 720 K; and (iii) two steps are due to the loss of phenyl groups [15] in the 720–920 K and 930–1270 K ranges, respectively, to give $\text{Ba}(\text{PO}_3)_2$ [23].

The differential scanning calorimetric curves at low temperature, shown in Figure 4, were employed to distinguish the hydrated and anhydrous lamellar com-

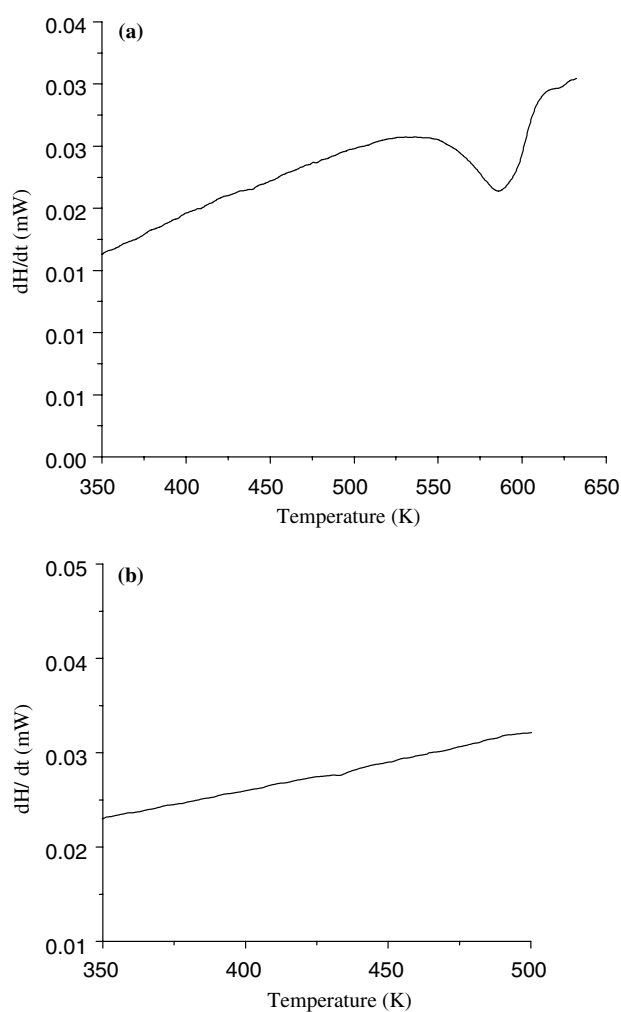


Figure 4. Differential scanning calorimetry for hydrated (a) and anhydrous (b) lamellar compounds.

pounds. Thus, the endothermic peak with the maximum centered at 580 K, shown in Figure 4a, is associated with the release of water molecules from the hydrated compound, which correlated with the mass loss on the thermogravimetric curve for this temperature region. However, only a base line was detected for the anhydrous compound in Figure 4b, as is expected, due to the absence of water of coordination.

Based on these TG and DSC curves, the anhydrous barium phenylphosphonate is clearly prepared from the crude synthetic product. On the other hand, this same dehydrating process was also confirmed after heating the hydrated compound at 520 K in vacuum for 8 h or by heating it in a muffle furnace for an identical time.

The scanning electron microscopic (SEM) photographs of the hydrated, anhydrous barium phenylphosphonate, and also for the sample intercalated with pentylamine are shown in Figure 5. The crystal morphology of these compounds is clearly lamellar, in good agreement with the expected structural characteristics. The morphology of intercalated pentylamine is very similar to that of the hydrated host matrix. These results are very important in order to obtain pillared compounds with a high degree of crystallinity.

Useful information related to phenylphosphonate group attachment on inorganic layers in the lamellar structure can be obtained through ^{31}P MAS NMR spectra, as illustrated for both hydrated and anhydrous compounds in Figure 6. The compounds presented a peak centered at 12.4 ppm, followed by a series of side bands. Thus, in the structures of compounds all cations should be equivalently distributed in the inorganic layers with coordination number eight, whose structure is stabilized by hydrogen bonds, by involving the free P—OH groups, as previously proposed [21]. The amine intercalation into hydrated barium phenylphosphonate showed a similar behavior as that observed for the anhydrous compound, and a single ^{31}P NMR peak centered at 12.0 ppm supports this fact.

An unequivocal confirmation about the phenylphosphonate group attachment on the inorganic structural layer is provided by a ^{13}C MAS NMR spectrum of the bonded phenylphosphonate, as shown in Figure 7, in which the structured carbon atoms on the ring are numbered as shown in the inserted phenyl structure. The assignments for the sequence of carbon atoms were proposed previously [22]. Thus, the series of peaks at 140, 138, 128 and 123 ppm, correspond to C¹, C² and C⁶, C⁴, C³ and C⁵, respectively.

The series of isotherms involving *n*-alkylamine intercalations on hydrated barium phenylphosphonate is shown Figure 8. The maximum number of moles of the amines intercalated was 1.06, 0.89, 0.80, 0.78 and 0.56 mmol g⁻¹ for ethyl, propyl, butyl, pentyl and hexylamines, respectively. For the same process of intercalation on anhydrous barium phenylphosphonate, the corresponding isotherms are shown in Figure 9, giving the values 1.14, 0.98, 0.95, 0.85 and 0.63 mmol g⁻¹ for the same sequence of guest molecules. To evaluate the

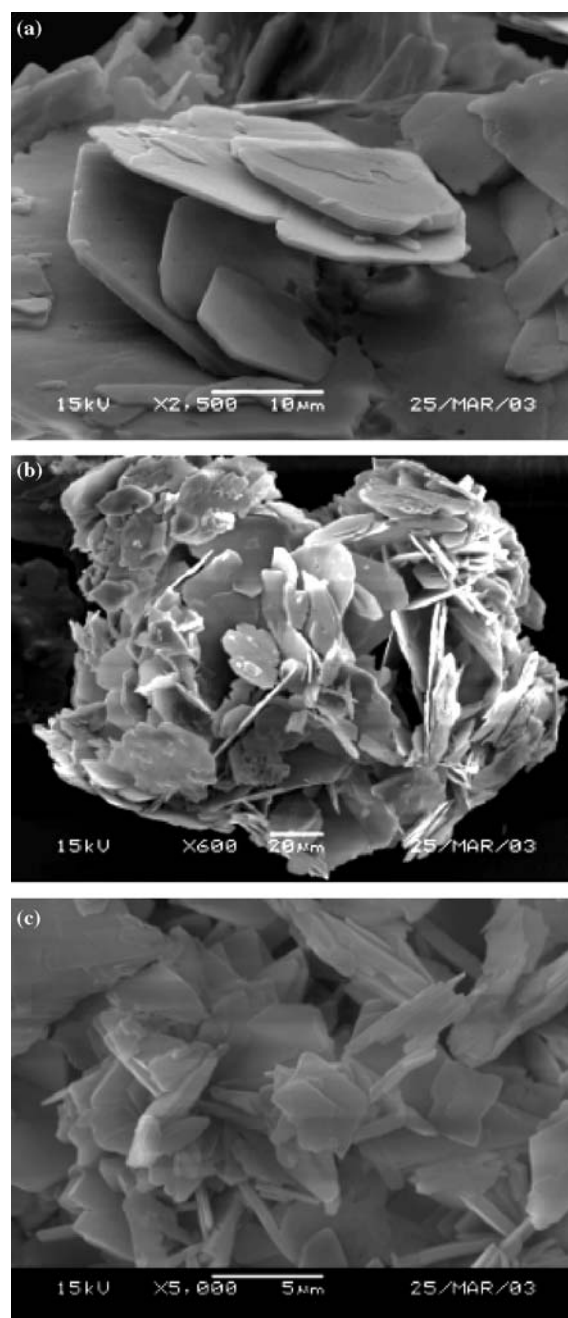


Figure 5. SEM photographs of hydrated barium phenylphosphonate (a), anhydrous barium phenylphosphonate (b) and intercalated with pentylamine (c).

data obtained from the isotherms in attempting to determine the amine molar fraction in solution, the results were adjusted to a Langmuir model, in which it is assumed that a monolayer of amines is formed on the inorganic matrix [23, 29–31], and the data were adjusted to expression (1):

$$C_s/n_f = C_s/n_s + 1/bn_s, \quad (1)$$

where C_s and n_f are the number of moles of the amine in the supernatant and intercalated, per gram of the barium phenylphosphonate, at each point of the titration, n_s is the amount of amine necessary to form

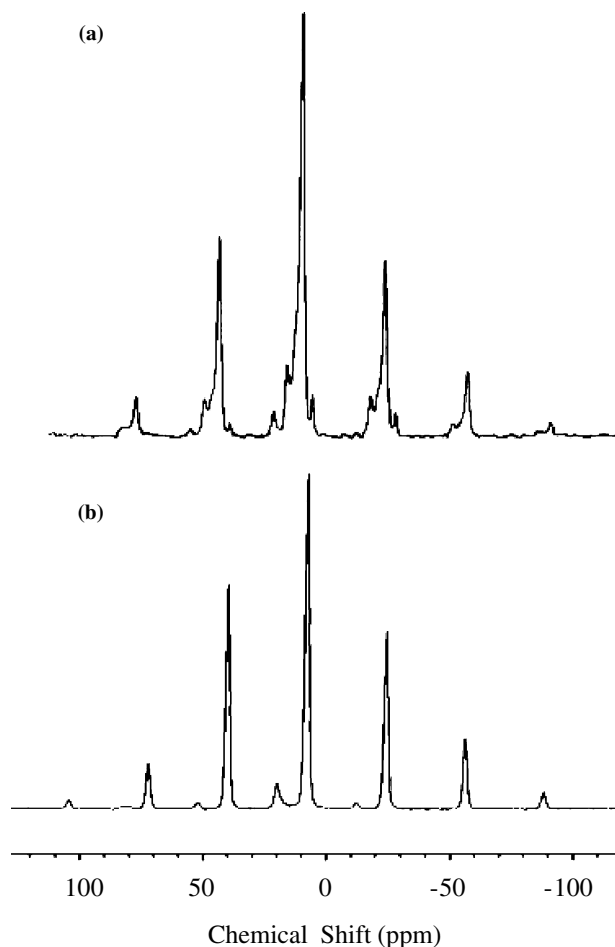


Figure 6. ^{31}P MAS NMR spectra of hydrated (a) and anhydrous (b) lamellar compounds.

a monolayer, and b is a constant related to the intensity of the reaction [29, 30, 35]. The curve of the isotherm of adsorption for butylamine is shown in Figure 10.

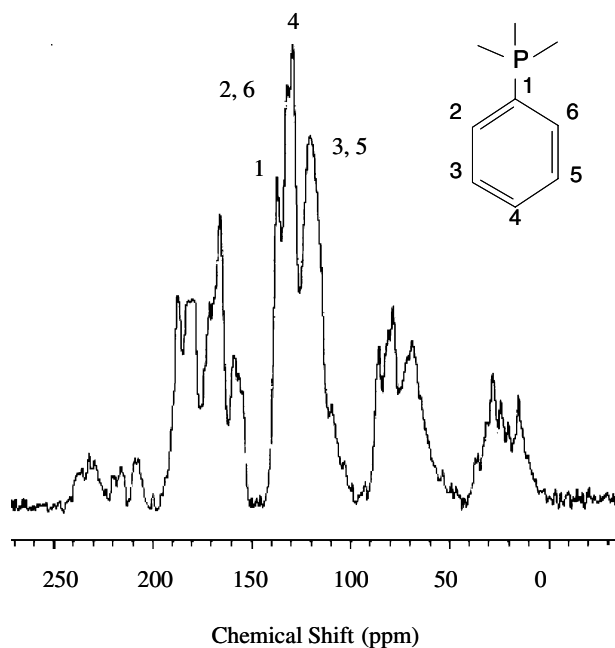


Figure 7. ^{13}C MAS NMR spectrum of the hydrated barium phenylphosphonate compound.

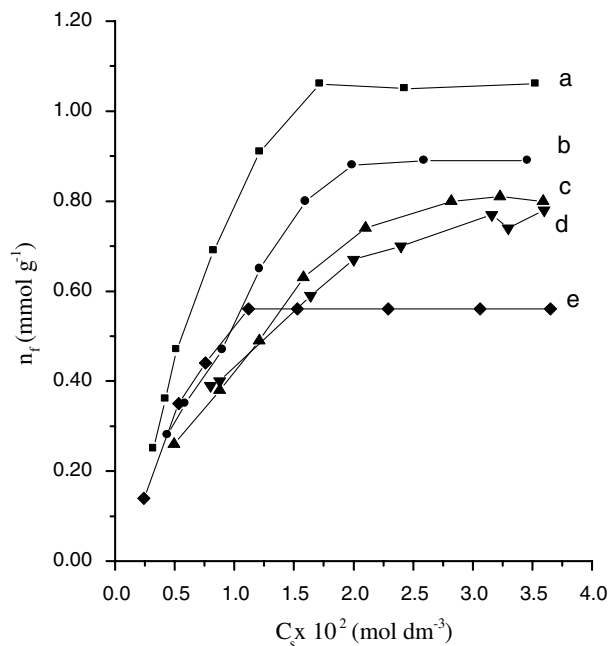


Figure 8. Isotherms of intercalation of hydrated barium phenylphosphonate with ethyl (a), propylamine (b), butyl (c), pentyl (d) and hexylamines (e).

The number of moles of the amine intercalated per gram (n_f) was higher for the anhydrous barium phenylphosphonate. This enhancement is a consequence of the increasing amounts of the available active sites on anhydrous barium phenylphosphonate, due to water removal. However, such experimental evidence conditions must consider hydrogen bond formation when the amine is dissolved in water. In such unfavorable conditions, the amine groups are highly solvated, a process which blocks the free available pair of electrons on the nitrogen atom from

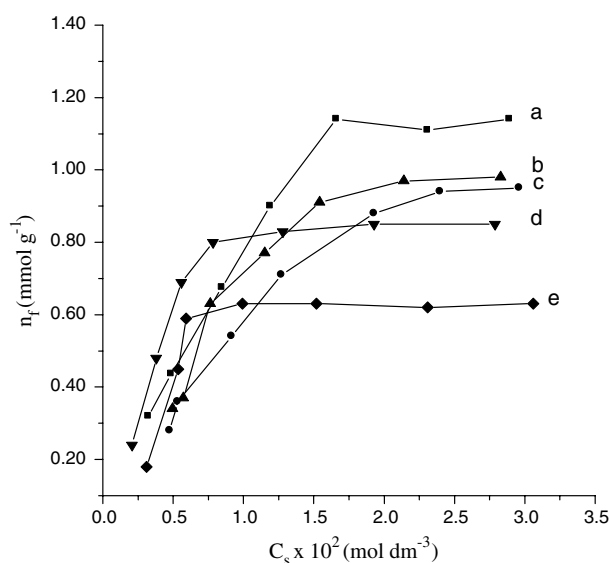


Figure 9. Isotherms of intercalation of anhydrous barium phenyl phosphonate with ethyl (a), propyl (b), butyl (c), pentyl (d) and hexylamines (e).

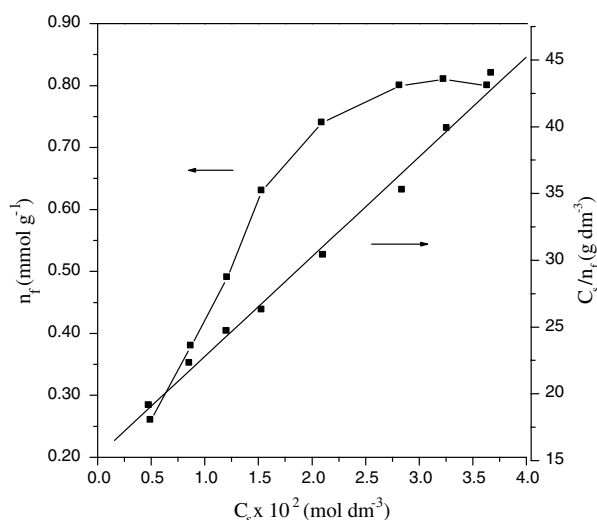


Figure 10. Isotherm of intercalation of butylamine into hydrated barium phenylphosphonate indicating (n_f) values vs. concentration (C_s). The straight line represents the linearization C_s/n_f vs. C_s . The coefficient of correlation r is 0.999.

bonding in the intercalating reaction. Based on this approach, an increase in the amine intercalating process should be expected in apolar solvents [31], as demonstrated by the present results.

The X-ray diffraction powder patterns for barium phenylphosphonate containing amines intercalated from aqueous solutions demonstrated clearly an increase in the interlayer distances caused by the entrance of the amines (Figure 1c), always with larger values than those observed for the original matrixes. Such an increase in interplanar distance correlates with the number of carbon atoms of the organic amine chains, as observed for other systems [30, 38–40], and the sequence of values for these distances are listed in Table 2. A common observation for all these reactions is connected to the change in crystallinity as observed before [23], when compared to that found for the original compound. It was supposed that the guest

Table 2. Interlayer distance (d) and surface area (S) for hydrated (BaPP) and anhydrous (BaPP1) barium phenylphosphonates and the n -alkylmonamine intercalated compounds

Compound	d (pm)	S ($\text{m}^2 \text{g}^{-1}$)
BaPP	1532	26.6 ± 0.3
BaPP $\cdot x\text{CH}_3\text{CH}_2\text{NH}_2 \cdot (1-x)\text{H}_2\text{O}$	1593	27.4 ± 0.3
BaPP $\cdot x\text{CH}_3(\text{CH}_2)_2\text{NH}_2 \cdot (1-x)\text{H}_2\text{O}$	1655	30.0 ± 0.4
BaPP $\cdot x\text{CH}_3(\text{CH}_2)_3\text{NH}_2 \cdot (1-x)\text{H}_2\text{O}$	1713	38.0 ± 0.5
BaPP $\cdot x\text{CH}_3(\text{CH}_2)_4\text{NH}_2 \cdot (1-x)\text{H}_2\text{O}$	1774	39.0 ± 0.4
BaPP $\cdot x\text{CH}_3(\text{CH}_2)_5\text{NH}_2 \cdot (1-x)\text{H}_2\text{O}$	1841	41.0 ± 0.5
BaPP1	1751	14.9 ± 0.4
BaPP1 $\cdot \text{CH}_3\text{CH}_2\text{NH}_2$	1811	15.8 ± 0.2
BaPP1 $\cdot \text{CH}_3(\text{CH}_2)_2\text{NH}_2$	1869	18.1 ± 0.3
BaPP1 $\cdot \text{CH}_3(\text{CH}_2)_3\text{NH}_2$	1929	25.1 ± 0.5
BaPP1 $\cdot \text{CH}_3(\text{CH}_2)_4\text{NH}_2$	1990	27.3 ± 0.4
BaPP1 $\cdot \text{CH}_3(\text{CH}_2)_5\text{NH}_2$	2053	28.6 ± 0.5

incorporation process seems to cause the elimination of possible irregularities in the original structure, to give the final well-formed peaks [16]. The relationship between the interlayer distance (d) and the number of carbons in the amine molecules (n_c) is shown in Figure 11 and is correlated to the following expressions, for the hydrated and anhydrous compounds, respectively:

$$d = 1467 + 62n_c \quad (2)$$

$$d = 1688 + 60n_c \quad (3)$$

Based on these expressions, the mean increase of the interlayer distance as a function of the number of carbons was found to be 62 and 60 pm, which is in good agreement with the value 57 pm, obtained when the same class of guest molecules is intercalated into calcium phenylphosphonate [22]. By considering the straight alkylamine chain in a normal trans–trans arrangement, the successive additions on increasing the chain length per carbon atom is estimated as 127 pm [41]. Then, the mean increase per carbon atom of 62 and 60 pm observed with the present compounds indicates that the alkyl chains must be arranged in bilayers tilted at a 30° angle ($\sin^{-1}\theta = 62/127$) or a 28° angle ($\sin^{-1}\theta = 60/127$) to the basal plane [42].

The quantitative degree of intercalation is confirmed by the increased amount of carbon and nitrogen percentages, in relation to the hydrated and anhydrous host matrices, as the amines are intercalated, as shown in Table 1. As mentioned, a close agreement between the

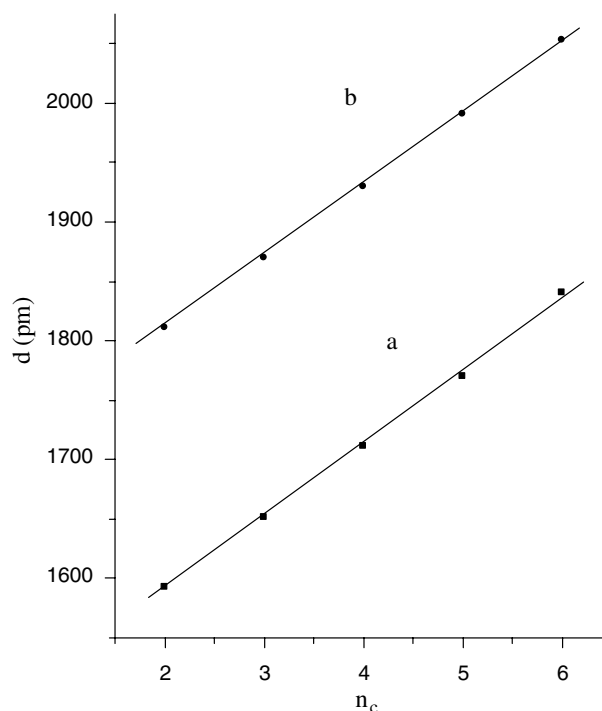


Figure 11. Interlayer distance vs. number of carbon atoms in the intercalated n -alkylamines: hydrated (a) and anhydrous (b) lamellar compounds.

calculated and observed elemental analyses is obtained for the original matrix. When the intercalation takes place, the bonded water molecules in the inorganic layer are partially replaced by the amine Lewis bases. Then, the listed values of carbon and hydrogen percentage obviously increase as the size of the amine chain increases, and, consequently, a decrease in nitrogen percentage is observed.

The surface area values and the corresponding interlamellar distances are listed in Table 2. The surface area of the original matrix, $26.6 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$, decreased to $14.9 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$ with water removal to give the anhydrous compound, with interlamellar distances of 1532 and 1751 pm for the original and anhydrous compounds, respectively. As observed, the presence of molecules inside the free lamellar cavity causes an increase in surface area. This behavior is also demonstrated by amine chain molecule addition, whose progressive increase in interlamellar distance is clearly demonstrated going from ethylamine up to the largest hexylamine molecule. In such conditions, the increase in surface area showed that amine interaction occurred on the inorganic support surface, which increase in distance enabled the entrance of the gaseous molecules during the area measurements.

Conclusions

Anhydrous and hydrated lamellar crystalline barium phenylphosphonates can be used as host support for organic polar molecules. From thermogravimetric data the hydrated compound contrasts with the anhydrous one, by showing a mass loss corresponding to a water molecule, a behavior which was confirmed through the DSC technique. From ^{31}P NMR, the hydrated form of this host compound presents one peak for bonded phenylphosphonate groups. From elemental analysis, the general formulas $\text{Ba}(\text{HO}_3\text{PC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{HO}_3\text{PC}_6\text{H}_5)_2$, for the hydrated and anhydrous compounds, respectively, were established.

The compounds showed high degrees of crystallinity, as observed through X-ray diffraction patterns. Amine intercalation causes an increase in the interlayer distance, while still maintaining the final lamellar structure being maintained. The interlayer distance correlates with the number of carbon atoms of the alkylamine chains through the expressions: $d = 1467 + 62n_c$ and $d = 1688 + 60n_c$, so that an unknown amine chain length can be inferred. The intercalated compounds presented an increase of carbon and hydrogen percentages as the size of the amine chain increased, with a corresponding decrease in nitrogen percentage, as observed through elemental analysis. During the intercalation processes the layered crystal structure of the inorganic matrix, as well as the morphology of the microcrystals, is basically maintained.

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References

1. A. Clearfield: *Prog. Inorg. Chem.* **47**, 371 (1998).
2. P. Capková and H. Schenk: *J. Incl. Phenom.* **47**, 1 (2003).
3. P. Capková, M. Pospíšil, and Z. Weiss: *J. Mol. Model.* **9**, 195 (2003).
4. G. Cao, H. Hong, and T.E. Mallouk: *Acc. Chem. Res.* **25**, 420 (1992).
5. M.E. Thompson: *Chem. Mater.* **6**, 1168 (1994).
6. A. Clearfield: *Comments Inorg. Chem.* **10**, 896 (1990).
7. G. Alberti and T. Bein (eds.), *Comprehensive Supramolecular Chemistry*, vol. 7, Pergamon Press: New York (1996).
8. M. Ogawa and K. Kuroda: *Chem. Rev.* **95**, 399 (1995).
9. U. Costantino, In A. Clearfield (ed.), *Inorganic Ion Exchange Materials*, CRC Press: Boca Raton (1982).
10. M.B. Dines and P. DiGiacomo: *Inorg. Chem.* **20**, 92 (1981).
11. K. Goubitz, P. Capková, K. Melánová, W. Molleman, and H. Schenk: *Acta Cryst.* **B57**, 178 (2001).
12. G.B. Hix, A. Turner, B.M. Kariuki, M. Tremayne, and E.J. MacLean: *J. Mater. Chem.* **12**, 3220 (2002).
13. N. Miyamoto, K. Kuroda, and M. Ogawa: *J. Mater. Chem.* **14**, 165 (2004).
14. M. Trchová, P. Capková, P. Matejka, K. Metánová, and L. Benes: *J. Solid State Chem.* **145**, 1 (1999).
15. V.M.A. García, E. Jaimez, A. Bortun, J.R. García, and J.J. Rodriguez: *Porous Mater.* **2**, 85 (1995).
16. J.L. Bideau, B. Bujoli, A. Jouanneaux, C. Payen, P. Palvadeau, and J. Rouxel: *Inorg. Chem.* **32**, 4617 (1993).
17. W. Liu, Y. Liu, Z. Shi, and W. Pang: *J. Mater. Chem.* **10**, 1451 (2000).
18. E. Jaimez, A. Bourton, G.B. Hix, J.R. García, J. Rodriguez, and R.C. T. Slate: *J. Chem. Soc. Dalton. Trans.* 285 (1996).
19. G. Alberti, U. Constantino, S. Alulli, and N. Tomassini: *J. Inorg. Nucl. Chem.* **40**, 113 (1978).
20. G. Cao, H. Lee, V.M. Lynch, and T.E. Mallouk: *Solid State Ionics* **26**, 63 (1988).
21. C.B.A. Lima and C. Airoidi: *Thermochim. Acta* **400**, 51 (2003).
22. C.B.A. Lima and C. Airoidi: *Solid State Sci.* **4**, 1321 (2002).
23. C.B.A. Lima and C. Airoidi: *Inter. J. Inorg. Chem.* **3**, 907 (2001).
24. D.M. Poojary, B. Zhang, A. Cabeza, M.A.G. Aranda, S. Bruque, and A. Clearfield: *J. Mater. Chem.* **6**, 639 (1996).
25. J.L. Bideau, C. Payen, P. Palvadeau, and B. Bujoli: *Inorg. Chem.* **33**, 4885 (1994).
26. D.M. Poojary, D. Grohol, and A. Clearfield: *Angew. Chem.* **34**, 1508 (1995).
27. L.N.H. Arakaki, L.M. Nunes, J.A. Simoni, and C. Airoidi: *J. Colloid Interface Sci.* **46**, 228 (2000).
28. M.G. Fonseca and C. Airoidi: *J. Mater. Chem.* **10**, 1457 (2000).
29. O.A. C. Monteiro Jr. and C. Airoidi: *J. Colloid Interface Sci.* **212**, 212 (1999).
30. C. Airoidi and S. Roca: *J. Mater. Chem.* **6**, 1963 (1996).
31. V.S. O. Ruiz and C. Airoidi: *J. Therm. Anal. Cal.* **71**, 459 (2003).
32. A.M. Lazarin, C.A. Borgo, Y.V. Kholin, and Y. Gushikem: *Anal. Chim. Acta* **477**, 305 (2003).
33. A.M. Lazarin, R. Landers, Y.V. Kholin, and Y. Gushikem: *J. Colloid Interface Sci.* **254**, 31 (2002).
34. C. Airoidi and S. Roca: *J. Solution Chem.* **22**, 707 (1993).
35. C. Airoidi and E.F. C. Alcântara: *J. Chem. Thermodyn.* **27**, 623 (1995).
36. M. Suarez, J.R. Garcia, and J. Rodrigues: *J. Mater. Chem. Phys.* **8**, 451 (1983).
37. S.F. Oliveira and C. Airoidi: *Mikrochim. Acta* **110**, 95 (1993).
38. C. Airoidi and S.F. Oliveira: *Structur. Chem.* **2**, 41 (1991).
39. C. Airoidi and D.S. Prandini: *Thermochim. Acta* **328**, 25 (1999).
40. L.M. Nunes and C. Airoidi: *J. Solid State Chem.* **154**, 557 (2000).
41. G. Lagaly: *Solid State Ionics* **22**, 43 (1986).
42. D.J. Machlan and K.R. Morgan: *J. Phys. Chem.* **94**, 7656 (1990).