

Intercalation behavior of calcium phenylphosphonate dihydrate $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$

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Abstract Intercalates of calcium phenylphosphonate dihydrate with 1-alkylamines (C_2 – C_{10}), 1-alkanols (C_3 – C_{10}), 1, ω -amino alcohols (C_2 – C_5), pyridine, morpholine, piperazine, aniline and 1-naphthylamine were prepared and characterized by powder X-ray diffraction and thermogravimetric analysis. The intercalates of alkanols and alkylamines are unstable at ambient conditions and the guest molecules are tilted to the host layers at an angle of 40° . The amino alcohol intercalates are stable and their basal spacings are very similar for all amino alcohols used and, in the case of ethanolamine and propanolamine, they contain co-intercalated water. Also arylamines and nitrogenous heterocycles form stable compounds. The general formula of these intercalates is $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot x\text{H}_2\text{O} \cdot y(\text{guest})$ and their basal spacings are from 15.39 to 15.78 Å.

Keywords Intercalation · Layered phenylphosphonate · Amines · Alkanols

Introduction

Inorganic-organic hybrid materials based on metal organophosphonates have been a subject of current interest owing to their potential applications in nonlinear optics, as catalysts, ion-exchangers, or molecular sensors [1]. Many of these compounds are layered ones and therefore can serve as hosts in intercalation reactions. From this point,

metal(IV) phosphonates, especially zirconium phosphonates were the most thoroughly studied [2]. On the other hand, organophosphonates of divalent metals, Me^{II} , have been studied to a much less extent. Regarding the organic part of these compounds one of the most common group prone to form layered structures is a phenyl group. First work, systematically describing phenylphosphonates of divalent metals with general formulae $\text{Me}^{\text{II}}\text{C}_6\text{H}_5\text{PO}_3$ and $\text{Me}^{\text{II}}\text{C}_6\text{H}_5\text{PO}_3 \cdot \text{H}_2\text{O}$ appeared in 1979 [3]. More detailed studies on Me^{II} phosphonates were published a decade later, in 1988 [4, 5]. First works, dealing with intercalations into layered Me^{II} phenylphosphonates, appeared in 1990s [6, 7].

Generally, there are two ways how these intercalation reactions are accomplished:

- (i) intercalation due to an acid-base interaction. In this case basic guest molecules (usually amines) are intercalated into metal hydrogen phosphonates in which their acid PO_3H groups interact with basic functional groups (e.g., $-\text{NH}_2$) of the guest. This can be denoted as a Brønsted-type intercalation. Examples are, for instance, intercalations of amines into calcium [8–10] and barium [11–13] hydrogen phenylphosphonates with the general formula $\text{Me}(\text{C}_6\text{H}_5\text{PO}_3\text{H})_2 \cdot y\text{H}_2\text{O}$ ($y = 0$ – 2).
- (ii) intercalation due to a coordination of a guest having a free electron pair to a metal having a free coordination site. This can be denoted as a Lewis-type intercalation. As examples, the intercalations of amines into zinc [14, 15], cadmium [16] or copper [7, 17] phenylphosphonates with the general formula $\text{MeC}_6\text{H}_5\text{PO}_3 \cdot \text{H}_2\text{O}$ can serve. The intercalates with zinc phenylphosphonates contain one amine molecule per formula unit. The amines coordinate to the zinc atoms at the site vacated by the water molecule and the alkyl chains are most

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likely packed as an interdigitated monolayer with a tilt angle of 78° with respect to the mean plane of the layer. On the other hand, two moles of amine are intercalated into copper phenylphosphonate [17].

Regarding phosphonates of alkaline-earth metals, the preparation and structures of hydrogen phenylphosphonates with the general formula $M(C_6H_5PO_3H)_2$ ($M = Ca, Sr, Ba$) were described [18–20]. Recently, we have prepared and characterized several new compounds with the general formula $MC_6H_5PO_3 \cdot 2H_2O$ ($M = Ca, Sr, Ba$) [21–23]. We found that these compounds can serve as hosts in intercalation reactions. In this paper, we describe the intercalation of 1-alkylamines, 1-alkanols, 1, ω -amino alcohols, nitrogenous heterocycles and arylamines into calcium phenylphosphonate dihydrate, $CaC_6H_5PO_3 \cdot 2H_2O$.

Experimental

The host material, $CaC_6H_5PO_3 \cdot 2H_2O$ (CaPhP), was prepared by precipitation from calcium salt and phenylphosphonic acid solutions with pH adjusted to 8.5 [21]. The guests used were obtained from Fluka or Aldrich. All aliphatic amines and amino alcohols were intercalated by stirring a suspension of CaPhP (0.1 g) in corresponding amine or amino alcohol (8 mL) at room temperature (in the case of ethylamine at $0^\circ C$) for 2 days. The intercalates of alcohols were prepared by suspending the butylamine intercalate (0.1 g) in corresponding alcohol (6 mL) and a subsequent short exposure (10–15 min) of the reaction mixture to a microwave field. Aniline, pyridine, and morpholine intercalates were prepared by stirring a suspension of CaPhP (0.1 g) in the corresponding guest (8 mL) at room temperature for 4 days. 1-Naphthylamine and piperazine were intercalated from toluene and acetonitrile saturated solutions, respectively.

Samples used for the XRD measurements contained small amounts of the free liquid guest and were covered with a protection foil to avoid deintercalation. Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXS, Germany) with Bragg-Brentano θ - θ geometry (40 kV, 40 mA) using $CuK\alpha$ radiation with secondary graphite monochromator. The diffraction angles were measured at room temperature from 2 to 37° (2θ) in 0.025° steps with a counting time of 2 s per step.

The thermogravimetric measurements were carried out in air between 30 and $960^\circ C$ at a heating rate of $5^\circ C\ min^{-1}$. Samples for the TG measurements were dried by an evaporation of the guest in an evacuated ampoule.

Infrared spectra were recorded on FT-IR spectrometer NEXUS (Nicolet, USA) in the range from 400 to $4,000\ cm^{-1}$ in nujol suspension.

Results and discussion

Intercalation of alkylamines and alkanols

In contrast to alkylamines, which can be easily intercalated at room temperature, alkanols cannot be directly intercalated into CaPhP. Only propanol can be intercalated by refluxing solid CaPhP in propanol. The other alkanols can be intercalated by a replacement of butylamine in the butylamine intercalate with corresponding alcohol in microwave field. Neither amines nor alkanols can be intercalated into anhydrous calcium phenylphosphonate.

All the intercalates prepared are white crystalline powders. The diffractograms of the intercalates contain a set of sharp basal reflections (see Fig. 1). Neither alkanol intercalates nor amine intercalates are stable in air. The stability of the intercalates decreases with increasing chain length, phases with lower basal spacing appear during washing the intercalates with toluene or hexane. New phases with lower basal spacing were also formed during the drying in an evacuated ampoule (see Fig. 2). The basal spacing of the propylamine intercalate dried in the ampoule is $15.87\ \text{\AA}$, and gradually decreases during the exposure to ambient air (30–35% relative humidity). After 20 min, a diffraction line corresponding to CaPhP appears and after 4 h the intercalate is completely transformed to parent CaPhP.

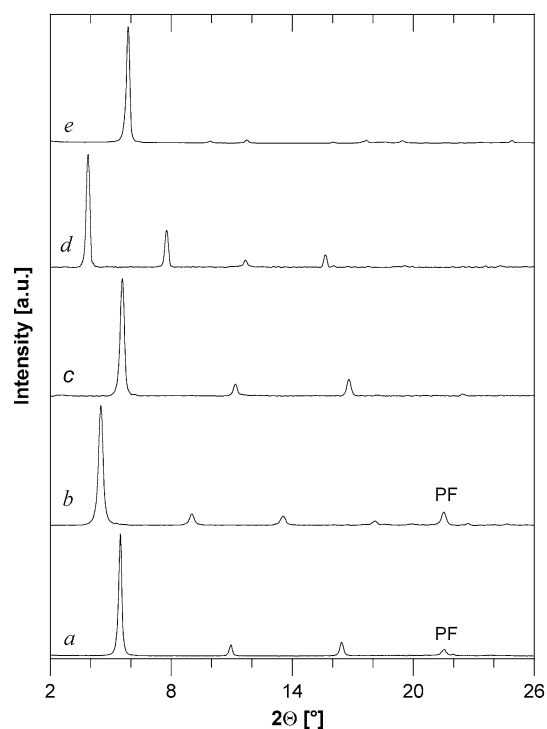


Fig. 1 The diffractograms of the CaPhP intercalates with propylamine (a), hexylamine (b), propanol (c), decanol (d) and parent host CaPhP·2H₂O (e). Peaks marked PF are from the polyethylene protecting foil

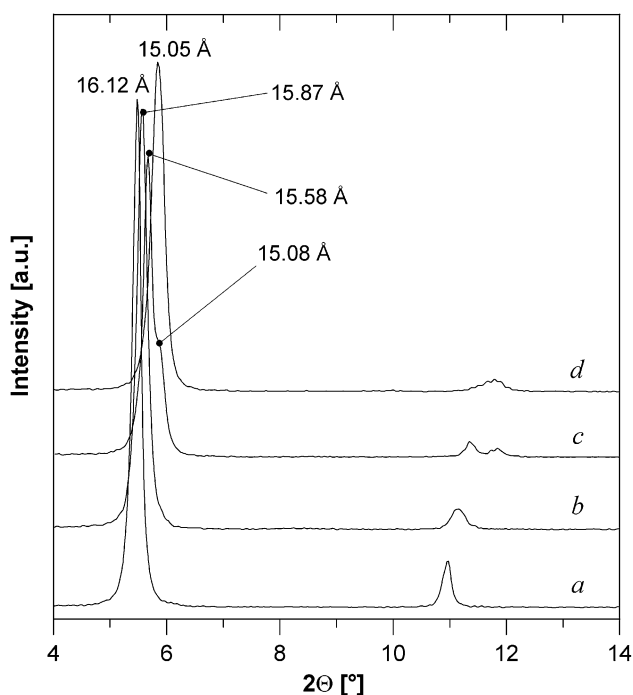


Fig. 2 The diffractograms of the as-prepared propylamine intercalate (a), the propylamine intercalate dried in evacuated ampoule (b), and after 20 min (c) and 4 h (d) at ambient conditions

On heating, the intercalates of alkanols lose weight in two steps, similarly as CaPhP [21]. As an example, the thermogravimetric curves of the intercalate with propanol is shown in Fig. 3a. The first weight loss of 16% is in the temperature range 100–210 °C, the second one of roughly

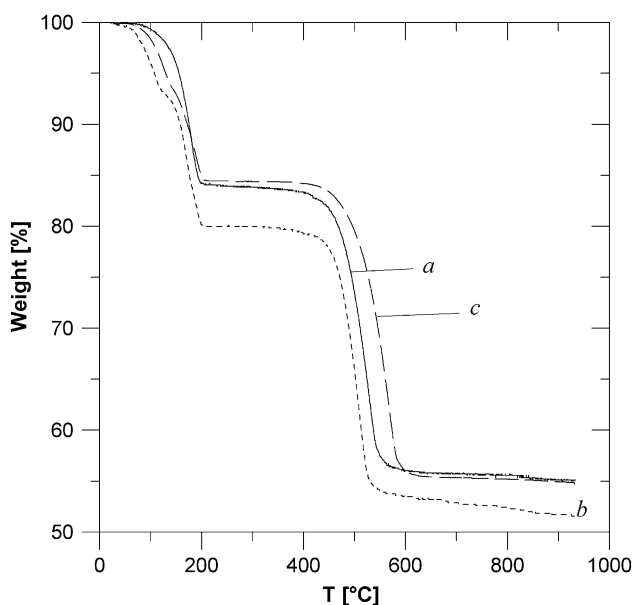


Fig. 3 TG curves of the propanol (a) and butylamine (b) intercalates and parent host CaPhP·2H₂O (c)

29% occurs from 400 to 600 °C. The slow decrease of weight above 600 °C (about 1%) is probably caused by slow burning of organic residues. Thus, the first weight loss corresponds to the release of propanol from CaC₆H₅PO₃·0.60C₃H₇OH (calculated weight loss of 15.5%), the second loss of weight is due to the decomposition of the phenylphosphonate (calculated weight loss of 29.8%). The product of heating to 950 °C is Ca₂P₂O₇, as confirmed by powder X-ray diffraction (PDF No. 09-345) [24]. On the other hand, the butylamine intercalate loses weight in three steps (see Fig. 3b). The first weight loss of 7% corresponds to the value calculated for the release of water from CaC₆H₅PO₃·0.45C₄H₉NH₂·H₂O (7.3%). The second weight loss of 13% corresponds to the butylamine release (theoretical value of 13.3%). The third weight loss (28%) corresponds to the decomposition of the phenylphosphonate group (calculated weight loss of 28.5%). The suggested formula is in accordance with elemental analysis: calcd.(%) C 37.92, H 4.88, N 2.55; found C 37.42, H 4.72, N 2.50. Similar formula CaC₆H₅PO₃·0.5C₃H₇NH₂·H₂O was determined for propylamine intercalate. We were not able to prepare dry samples of the intercalates of the longer alkanols and amines for thermogravimetric analyses even if they were carefully dried in an evacuated ampoule. Their X-ray powder patterns after drying always show phases with the basal spacing lower than that of the intercalate containing a small excess of the guest. As the alkanol content in these phases with lower basal spacing was in the range of 0.6–0.8 of the alkanol molecule per formula unit, we supposed that the ideal composition of the alkanol intercalates could be one guest molecule per CaC₆H₅PO₃. The alkylamine intercalates probably contain one water molecule and about a half of alkylamine molecule per CaC₆H₅PO₃.

The dependence of the basal spacing on the number of the carbon atoms in the guest chain is given in Fig. 4. In the case of the guests with more than four carbon atoms, the dependences are linear with the slope of 0.82 for both types of the intercalates. It means that the amine and alkanol molecules are probably arranged in a monomolecular way and their axes are tilted at an angle of 40° to the host layers. Ethylamine, propylamine and propanol molecules are probably arranged in other way. Similar phenomenon was also observed for alkanols intercalated VOPO₄ [25, 26].

IR spectra of propylamine and butanol intercalates were measured. As the propylamine and butanol intercalates are not stable they must be measured in nujol suspension. The bands of aliphatic chains were overlapped by nujol bands. The C–O stretching vibration of butanol in the spectrum of the intercalate was overlapped by bands from phosphonate groups. In the case of propylamine intercalate, there is a very broad band at about 1630 cm⁻¹ so we were not able to distinguish between the bands coming from NH₂ group and from cointercalated water.

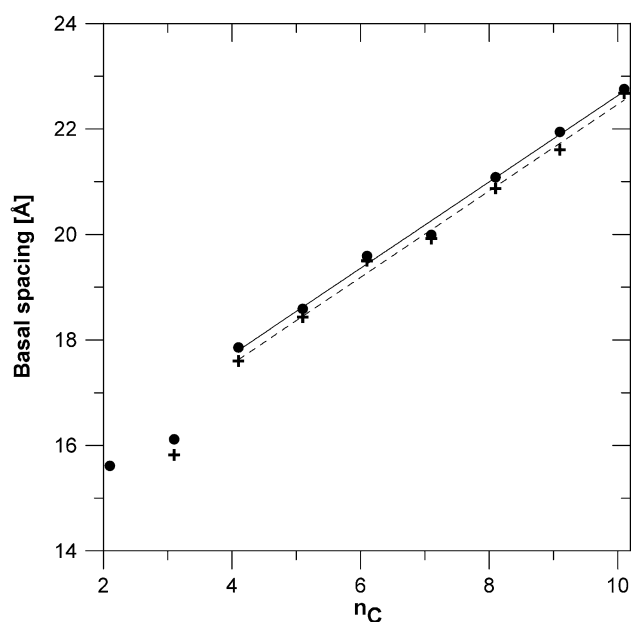


Fig. 4 The dependence of the basal spacing d of the intercalates of the alkylamines (circles) and alkanols (crosses) on the number of carbon atoms n_C

Intercalation of amino alcohols

In contrast to the intercalates of amines and alkanols, the intercalates of amino alcohols are stable at ambient conditions. The diffractograms of the intercalates contain a series of sharp basal reflections and the basal spacings of the intercalates are very similar for all amino alcohols used (see Table 1). The diffractograms of the propanolamine and the butanolamine intercalates together with their TG curves are given in Fig. 5. The formula of the propanolamine intercalate $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot 1.0\text{H}_2\text{O} \cdot 0.50\text{HOC}_3\text{H}_6\text{NH}_2$ was suggested on the basis of elemental analysis (see Table 1). The propanolamine intercalate loses weight in three steps but the individual weight losses cannot be clearly separated. The first weight loss of about 7.0% is in the temperature range 80–150 °C, the second one of roughly 15% occurs from 150 to 300 °C and the third one of about 27% is above 300 °C. Thus, the first weight loss corresponds to the release of water (calculated weight loss

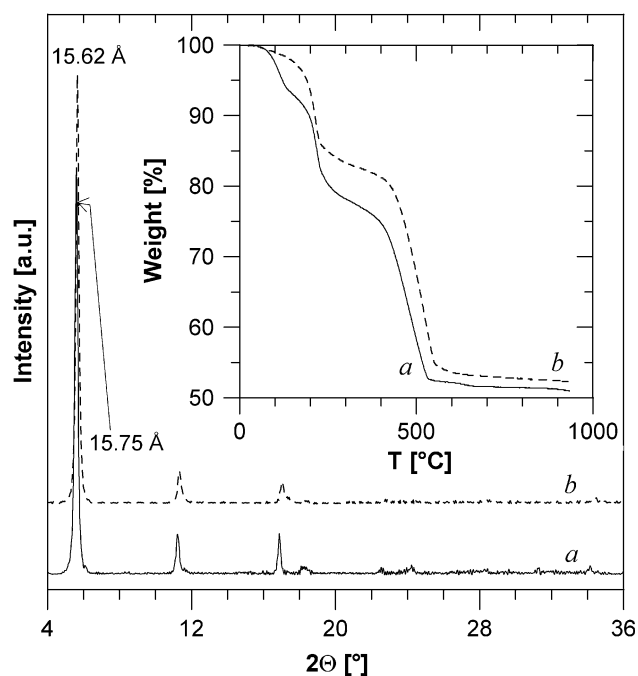


Fig. 5 Diffractograms of the propanolamine (a) and butanolamine (b) intercalates. Corresponding TG curves are given in the inset

of 7.2%), the second one corresponds to the release of propanolamine (calculated weight loss of 14.9%), and the third one is due to the decomposition of the phenylphosphonate (calculated weight loss of 27.4%). The ethanolamine intercalate decomposes similarly.

On the other hand, butanolamine intercalate $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot 0.48\text{HOC}_4\text{H}_8\text{NH}_2$ loses weight in two steps. The first weight loss of about 17% up to 320 °C corresponds to the release of butanolamine (calculated value of 17.9%) and the second weight loss of about 30% is due to the decomposition of the phenylphosphonate (calculated value 28.9%). The pentanolamine intercalate decomposes similarly.

As the structure of the parent host is not known it is very difficult to suggest the arrangement of the guest molecules. Taking similarity of the basal spacings of all the amino alcohol intercalates into account, we suppose that either the amino alcohol molecules can be arranged parallel to the

Table 1 The basal spacings and stoichiometric quotients of the $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot x\text{H}_2\text{O} \cdot y(\text{aminoalcohol})$ intercalates and the results of elemental analysis

Aminoalcohol	Basal spacing [Å]	x	y	Analysis [%] found/calculated		
				C	H	N
Ethanolamine	15.65	1.0	0.50	32.05/32.25	4.15/4.06	2.60/2.69
Propanolamine	15.75	1.0	0.50	35.05/35.79	4.55/4.61	2.90/2.78
Butanolamine	15.62	0.0	0.48	40.07/39.81	4.45/4.34	2.81/2.76
Pentanolamine	15.47	0.0	0.33	37.25/37.32	3.74/3.80	2.02/1.88

Table 2 The basal spacings, stoichiometric quotients of the $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot x\text{H}_2\text{O} \cdot y(\text{guest})$ intercalates, their elemental analysis and thermogravimetric analysis

Guest	Basal spacing [Å]	x	y	Analysis [%] found/calcd.			Weight loss [%] found/calcd.		
				C	H	N	Δw_1	Δw_2	Δw_3
Pyridine	15.78	0.5	0.5	40.82/41.72	3.62/3.50	2.82/2.86	4.0/3.7	16.5/16.2	26.5/28.2
Morpholine	15.61	1.0	0.35	36.66/36.33	4.41/4.18	1.80/2.00	7.0/7.4	13.0/12.5	29.0/28.2
Piperazine	15.69	1.0	0.34	36.27/36.31	4.17/4.31	3.86/3.91	7.0/7.4	11.5/12.0	28.0/28.4
Aniline	15.64	1.0	0.28	37.88/38.40	3.99/3.76	1.52/1.63	7.0/7.5	11.5/10.9	29.0/28.7
1-Naphthylamine	15.39	1.0	0.12	37.02/37.38	3.63/3.52	0.75/0.73	8.0/7.8	7.0/7.4	28.0/29.8

host layers or they can fill some cavities in the structure. The parallel arrangement of the amino alcohol molecules and the presence of the functional groups on both ends of the aliphatic chain are probably the reason for higher stability of the amino alcohol intercalates in comparison with the aliphatic amine or alcohol intercalates.

Intercalation of nitrogenous heterocycles and arylamines

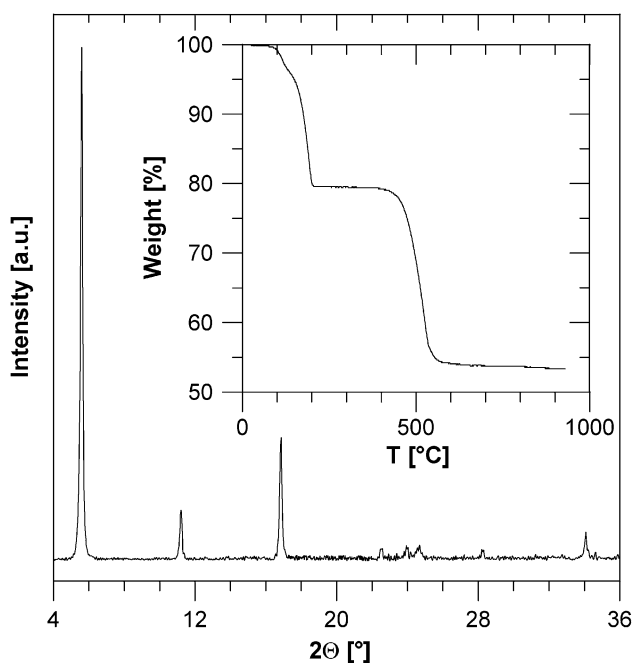
The intercalates of pyridine, morpholine, piperazine, aniline and 1-naphthylamine are also stable at ambient conditions. The diffractograms of the intercalates contain series of sharp basal reflections and the basal spacings of the intercalates are very similar for all guests used (see Table 2). As an example, the diffractogram of the pyridine intercalate together with its TG curve is given in Fig. 6. The intercalate loses weight in three steps. The first weight

loss of about 4% up to 120 °C corresponds to the release of water (calculated value of 3.7%) and the second weight loss of about 16.5% corresponds to the release of intercalated pyridine (calculated value of 16.2%). The third weight loss of 26.5% is due to the decomposition of the phenylphosphonate (calculated value of 28.2%). The intercalates of other heterocycles and aromatic amines decompose similarly. Their formulas and basal spacings are given in Table 2. IR spectrum of the pyridine intercalate was measured. We are not able to determine the way of pyridine bonding because pyridine bands cannot be distinguished from bands of the phenyl group.

Conclusion

Even though the structure of $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$ is not determined yet, this compound can be used as a layered host material able to intercalate organic molecules having suitable functional groups. In contrast to calcium hydrogen phosphonate intercalates, where amine molecules interact with acid PO_3H group and are protonated, the guest molecules in the calcium phenylphosphonate can be held either by Lewis interaction or by van der Waals interaction. Alkanols form intercalates with the general formula $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot x(\text{alkanol})$. On the other hand, alkylamines form intercalates containing water with general formula $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot x(\text{alkylamine}) \cdot \text{H}_2\text{O}$. Due the instability of the intercalates, the value of x could not be determined. Amino alcohols form stable intercalates with the general formula $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot \text{H}_2\text{O} \cdot 0.5\text{HO}(\text{CH}_2)_n\text{NH}_2$ ($n = 2$ or 3) or $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot x\text{HO}(\text{CH}_2)_n\text{NH}_2$ (where $x = 0.48$ for $n = 4$ and $x = 0.33$ for $n = 5$). Also arylamines and nitrogenous heterocycles form stable compounds with the general formula $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot x\text{H}_2\text{O} \cdot y(\text{guest})$. In the case of heterocycles and arylamines we can presume that there is an interaction between the conjugated double bond systems of the guest and the benzene ring of the host which can increase the stability of these intercalates.

The ability of $\text{CaC}_6\text{H}_5\text{PO}_3 \cdot 2\text{H}_2\text{O}$ to intercalate amines and alcohols can be applied in anchoring in their interlayer

**Fig. 6** Diffractogram and TG curve of the pyridine intercalate

space commercially interesting, e.g., optically or pharmaceutically active molecules.

The instability of some of the prepared intercalates seems to be a drawback in their utilization. On the other hand, this instability can be employed for a directed release of the intercalated species, when desirable.

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References

1. Alberti, G.: Layered metal phosphonates and covalently pillared diphosphonates. In Atwood, J.L., Davies, J.E.D., MacNicol, D.D., Vögtle, F. (eds.) *Comprehensive Supramolecular Chemistry*, vol. 7, pp. 151–187. Pergamon, Oxford (1996)
2. Cao, G., Lee, H., Lynch, V.M., Mallouk, T.E.: Synthesis and structural characterization of a homologous series of divalent metal phosphonates, $M^{II}(O_3PR)\cdot H_2O$ and $M^{II}(HO_3PR)_2$. *Inorg. Chem.* **27**, 2781–2785 (1988)
3. Cunningham, D., Hennelly, P.J.D., Deeney, T.: Divalent metal phenylphosphonates and phenylarsonates. *Inorg. Chim. Acta* **37**, 95–102 (1979)
4. Cao, G., Lee, H., Lynch, V.M., Mallouk, T.E.: Structural studies of some new lamellar magnesium, manganese and calcium phosphonates. *Solid State Ion.* **26**, 63–69 (1988)
5. Cao, G., Lynch, V.M., Swinnea, J.S., Mallouk, T.E.: Synthesis and structural characterization of layered calcium and lanthanide phosphonate salts. *Inorg. Chem.* **29**, 2112–2117 (1990)
6. Cao, G., Mallouk, T.E.: Shape-selective intercalation reactions of layered zinc and cobalt phosphonates. *Inorg. Chem.* **30**, 1434–1438 (1991)
7. Zhang, Y.P., Clearfield, A.: Synthesis, crystal structures, and coordination intercalation behavior of two copper phosphonates. *Inorg. Chem.* **31**, 2821–2826 (1992)
8. Lima, C.B.A., Airoidi, C.: Layered crystalline calcium phenylphosphonate-synthesis, characterization and n-alkylmonoamine intercalation. *Solid State Sci.* **4**, 1321–1329 (2002)
9. Lazarin, A.M., Airoidi, C.: Calorimetric data on n-alkyldiamines intercalated into calcium phenylphosphonates. *Thermochim. Acta* **437**, 114–120 (2005)
10. Lima, C.B.A., Airoidi, C.: Crystalline calcium phenylphosphonate-thermodynamic data on n-alkylmonoamine intercalations. *Thermochim. Acta* **400**, 51–59 (2003)
11. Lazarin, A.M., Airoidi, C.: Layered crystalline barium phenylphosphonate as host support for n-alkylmonoamine intercalation. *J. Incl. Phenom. Macrocycl. Chem.* **51**, 33–40 (2005)
12. Lazarin, A.M., Lima, I.S., Simoni, J.A., Airoidi, C.: Crystalline-hydrated barium phenylphosphonate as a host for n-alkyldiamine intercalation. *J. Mater. Res.* **21**, 2191–2197 (2006)
13. Lazarin, A.M., Airoidi, C.: Host hydrated barium phenylphosphonate/guest heterocyclic amine intercalation energetics by calorimetric titration. *Thermochim. Acta* **445**, 57–60 (2006)
14. Zhang, Y.P., Scott, K.J., Clearfield, A.: Intercalation of alkylamines into dehydrated and hydrated zinc phenylphosphonates. *J. Mater. Chem.* **5**, 315–318 (1995)
15. Poojary, D.M., Clearfield, A.: Coordinative intercalation of alkylamines into layered zinc phenylphosphonate. Crystal structures from X-ray powder diffraction data. *J. Am. Chem. Soc.* **117**, 11278–11284 (1995)
16. Cao, G., Lynch, V.M., Yacullo, L.N.: Synthesis, structural characterization, and intercalation chemistry of two layered cadmium organophosphonates. *Chem. Mater.* **5**, 1000–1006 (1993)
17. Zhang, Y.P., Scott, K.J., Clearfield, A.: Intercalation of alkylamines into layered copper phosphonates. *Chem. Mater.* **5**, 459–499 (1993)
18. Mahmoudkani, A.H., Langer, V.: Layered calcium phenylphosphonate: synthesis and properties. *Solid State Sci.* **3**, 519–525 (2001)
19. Mahmoudkani, A.H., Langer, V., Smrčok, L.: Layered strontium phenylphosphonate: synthesis, thermal properties and crystal structure from X-ray powder diffraction data. *Solid State Sci.* **4**, 873–878 (2002)
20. Poojary, D.M., Zhang, B., Cabeza, A., Aranda, M.A.G., Bruque, S., Clearfield, A.: Synthesis and crystal structures of two metal phosphonates, $M(HO_3PC_6H_5)_2$ ($M = Ba, Pb$). *J. Mater. Chem.* **6**, 639–644 (1996)
21. Svoboda, J., Zima, V., Beneš, L., Melánová, K., Vlček, M.: Synthesis and characterization of new calcium phenylphosphonates and 4-carboxyphenylphosphonates. *Inorg. Chem.* **44**, 9968–9976 (2005)
22. Zima, V., Svoboda, J., Beneš, L., Melánová, K., Trchová, M.: New strontium phenylphosphonate: synthesis and characterization. *Solid State Sci.* **8**, 1380–1385 (2006)
23. Svoboda, J., Zima, V., Beneš, L., Melánová, K., Vlček, M., Trchová, M.: Synthesis and characterization of new potential intercalation hosts-barium arylphosphonates. *J. Phys. Chem. Solids* **69**, 1439–1443 (2008)
24. Joint Committee on Powder Diffraction Standards, International Centre of Diffraction Data, Swarthmore, PA
25. Čapková, P., Melánová, K., Beneš, L., Schenk, H.: Modeling in structure analysis of vanadyl phosphate intercalated with 1-alkanols. *J. Mol. Model.* **6**, 9–15 (2000)
26. Beneš, L., Zima, V., Melánová, K.: 2-Alkanol intercalated $VOPO_4$ and $NbOPO_4$: structure modeling of intercalate layers. *J. Incl. Phenom. Macrocycl. Chem.* **40**, 131–138 (2001)