



$(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$: Hydrothermal Synthesis and Reaction with *n*-Alkylamine Vapours

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(Received: 13 March 2003; in final form: 31 December 2003)

Key words: *n*-alkylamines, sorption, zinc phosphates

Abstract

$(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ was synthesized under mild hydrothermal conditions in the presence of urea. The reaction with *n*-alkylamines has been investigated by exposing the solid to amines vapor. The new materials were characterized by chemical and thermal analysis, powder X-ray diffraction, and IR spectroscopy. In addition, the simultaneous reaction of this compound with two or more *n*-alkylamine different molecules was investigated. The reaction of large *n*-alkylamine molecules was observed to be faster if there is a shorter alkyl chain amine acting as a catalyst, yielding on completion single amine materials. In the case of a vapor mixture of several amines, the compound obtained depends on the reaction time.

Introduction

Polyvalent metal phosphates have been extensively studied in recent decades. In fact, these compounds present many properties that make them very interesting in some applications such as ion-exchange, intercalation, catalysis and ionic conductivity. As a result of progress in the synthesis of molecular sieves (zeolites, aluminophosphates, silicoaluminophosphates and so on) using soft-chemistry methods (mostly the hydrothermal technique), research into the metal salts of phosphoric acid has been widely developed so as to obtain crystalline compounds with a regular porous structure. The hydrothermal technique has been used successfully for the synthesis of zeolites [1, 2], phosphates [3–11], arsenates [12, 13] and certain metal oxides [14–16].

Several new compounds in the zinc phosphates family have recently been synthesised by the hydrothermal method [17–22]. Small organic molecules, particularly those containing amino groups, have played an out-standing role in templating novel networks [23–30]. In some cases, there is a striking, beautiful relationship between the template's shape and the surrounding framework topology [31]. For example, the uses of quiral molecules such as d-glucosamide in the synthesis of zinc phosphates enables new materials to have enantioselective properties and may have applications in such diverse fields as the pharmaceutical and medical industries [32]. It is also known the synthesis of lamellar zinc phosphates from aqueous solutions containing ammonium bromide surfactants [33, 34] as well as the preparation of layered zincophosphate materials obtained via thermolysis in anhydrous organic solvents in the presence of long-chain primary amines [35].

In addition to their possible use as molecular sieves, metal phosphate/*n*-alkylamine materials seem to be useful as

precursors in pillaring reactions owing to their stability in the aqueous medium, suitable interlayer distance and moderate affinity of the organic species toward the active centres of the host [36, 37]. For this reason, the structure of these materials should be considered. The reaction of *n*-alkylamines in the vapor phase into metal phosphates is a spontaneous process in which each amino group of the organic compound interacts with one hydrogen of the phosphate group, giving rise to a stable bonding. The process rate decreases as the length of the amine alkyl chain increases. Thus, the reaction of long-chain amines is a very time-demanding process [38]. The coexistence of a short-chain amine with a larger one should favour intercalation kinetics: the presence of a small amine can reduce the activation energy for the intercalation of a large one by opening the phosphate layers [39].

The single crystal structure of a new ammonium zinc phosphate, $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$, has recently been reported by Bircsak and Harrison [40]. This compound (triclinic, space group P-1) is layered with respect to zinc-phosphorus-oxygen connectivity (see Figure 1). The Zn and P atoms both adopt tetrahedral coordination. Six of the eight unique O atoms form bicoordinate Zn–O–P bridges, one O atom is trigonally coordinated, and the remaining O atom forms part of a terminal P–OH bond. The polyhedral connectivity of the tetrahedral units results in corrugated anionic layers of stoichiometry $[\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)]^-$. Extra-layer NH_4^+ cations complete the crystal structure of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$. The chemical and structural characteristics of this material make it potentially interesting in fields such as intercalation, ion exchange and proton conduction.

In the recent past, $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ has been obtained as a sub-product from hydrothermal synthesis starting from a ZnO, V_2O_5 , VCl_3 , $[\text{C}(\text{NH}_2)_3]\text{CO}_3$, H_3PO_4 and H_2O mixture [40]. To date, there have been no reports of syn-

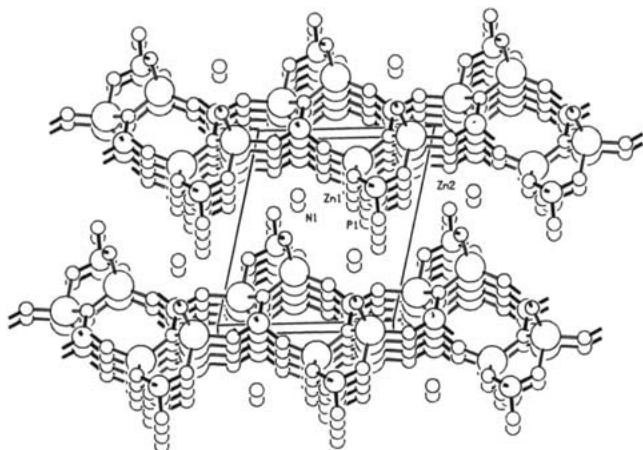


Figure 1. View of the $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ structure down [100].

thesis of the unique compound. Here, we report the first synthesis of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ as a unique product and the evolution of this compound during the reaction with linear monoamine vapors.

Experimental

Materials

All chemicals used were of reagent grade (Merck) and were employed without further purification. Hydrothermal crystallization of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ was carried out in a stainless steel autoclave with a Teflon liner under autogenous pressure. $(\text{NH}_2)_2\text{CO}$ (solid), 5 M H_3PO_4 and ZnCl_2 (solid) were mixed in the molar ratio 1:1:1:55 ($\text{ZnCl}_2:\text{H}_3\text{PO}_4:(\text{NH}_2)_2\text{CO}:\text{H}_2\text{O}$) in a total volume of 70 cm^3 . The autoclave was sealed and heated in an oven at 180 °C for 7 days. After cooling, the product was filtered, washed with distilled water and dried in air at room temperature. The crystals obtained (Figure 2) were ground to a particle size of less than 0.045 mm.

Reaction procedure

Compounds with amines were obtained by placing $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ in an atmosphere saturated with amine vapors at room temperature. The time needed to reach saturation is a function of the alkyl chain length (as well as the particle size) of the amines. The samples were air dried at 50 °C and stored over an aqueous solution of 50% H_2SO_4 .

Analytical procedure

The diffractometer used was a Philips PW1729/1720 model with $\text{CuK}\alpha$ ($\lambda = 1.5418\text{\AA}$) radiation. Indexing of the X-ray powder diffraction pattern was performed with the program KOHL [41] which is part of the CRYSFIRE indexing suite [42] starting from well-resolved peak diffraction positions. Microanalytical data (C, N and H) was obtained using a Perkin-Elmer model 2400B elemental analyzer. Infrared spectra were recorded with a Perkin-Elmer 1000

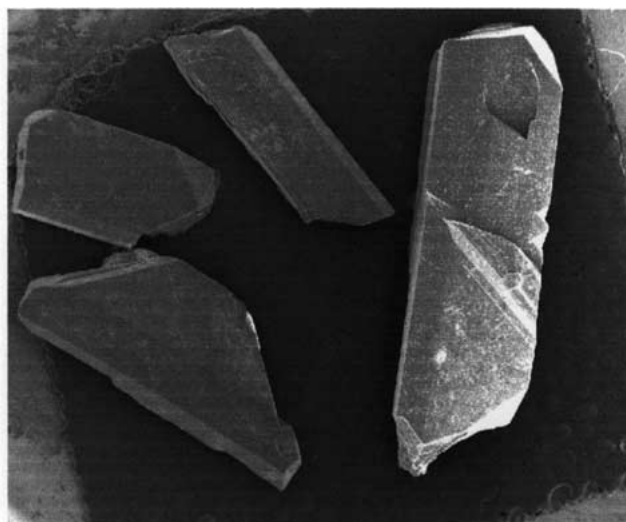


Figure 2. SEM image of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ (12 \times magnification).

FT-IR spectrophotometer. Thermal analysis was performed with a Mettler TA 4000 (TG 50, DSC 30, under nitrogen, heating rate 10 °C min^{-1}). Phosphorous and zinc contents were determined using a SpectraSpectrometer DCP-AEC after dissolving a weighed amount of the sample in $\text{HF}(\text{aq})$. Electron micrographs were recorded with a JEOL JSM 6100 scanning electron microscope operating at 20 kV.

Results and discussion

Synthesis and characterization of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$

The powder X-ray diffractogram of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ is shown in Figure 3a. It is similar to that of the material previously reported [39], with an interlayer distance of 9.18 \AA . The experimental analytical data: 38.3% Zn, 18.4% P, 4.0% N and 1.3% H (calcd. for $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$: 38.5% Zn, 18.3% P, 4.1% N and 1.5% H), is consistent with this composition. Figure 4a shows the infrared spectra of this compound. The presence of protonated ammonium groups manifests itself as a strong band at 1450 cm^{-1} . The bands in the region 900–1200 cm^{-1} are assigned to symmetric and antisymmetric stretching modes of P–O bonds in the PO_4 group, while the bands in the region 2750–3300 cm^{-1} arise from the P–OH and N–H bonds. Figure 5 contains the TG and DTG curves for $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$, and show that the weight loss up to 1000 °C was 10.5% (calcd. 10.30). The thermal decomposition takes place in two principal steps. The first stage (ca. 370 °C) is related to the loss of ammonia and 80% of condensation water, with formation of a mixture of $\gamma\text{-Zn}_2\text{P}_2\text{O}_7$, $\text{ZnH}_2\text{P}_2\text{O}_7$ and ZnO [43–45]. Water loss is completed in the last step (ca. 480 °C). After cooling, the final product of thermal treatment is $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$ [46]. The DSC curve (Figure 5) is in good agreement with the above findings, showing three endothermic bands at 390, 415 and 520 °C; the first two are related to the loss of ammonia and

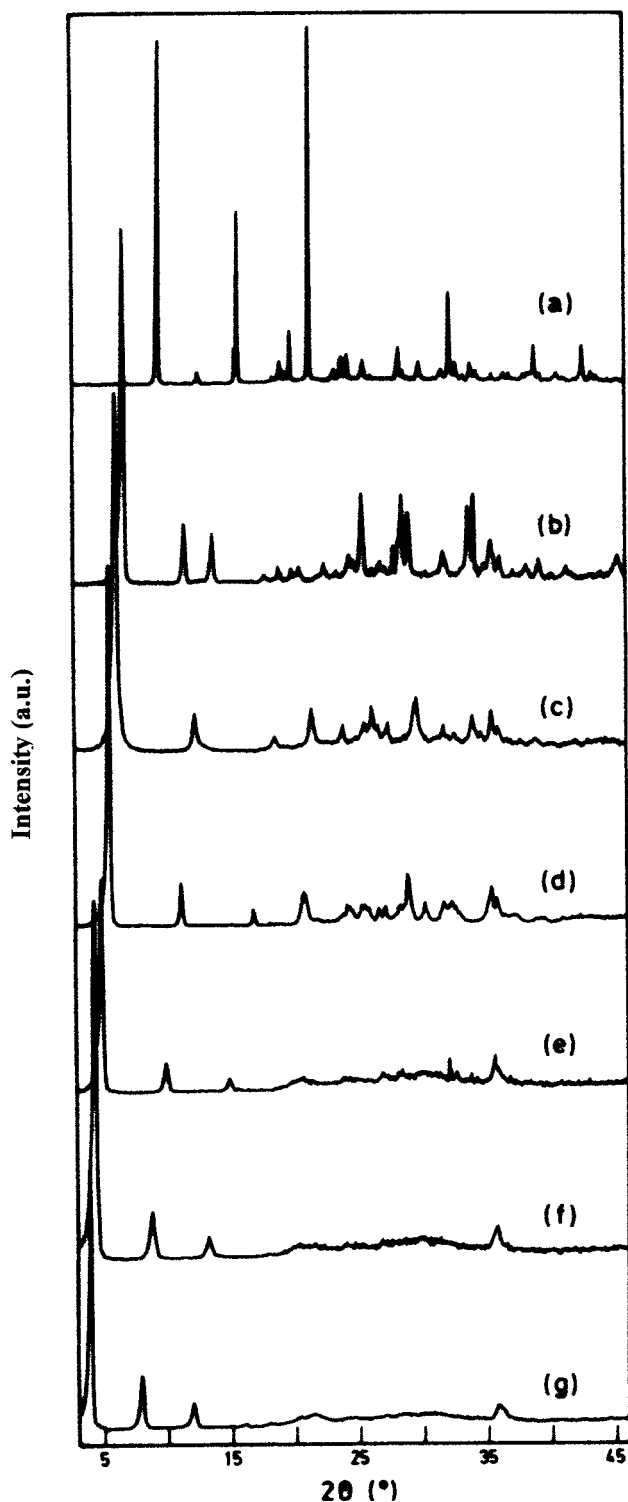


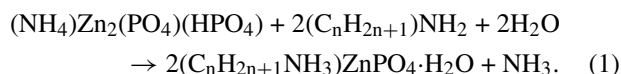
Figure 3. Powder X-ray diffraction patterns of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ (a), and its reaction compounds with methyl- (b), ethyl- (c), propyl- (d), *n*-butyl- (e), *n*-pentyl- (f), and *n*-hexylamine (g).

a high percentage of the condensation water. Water loss is completed in the third step.

Reaction with *n*-alkylamines

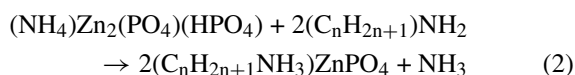
The reaction of methylamine vapors into $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ develops rapidly. The analysis data (Table 1) indicates the formation of a monohydrated saturated phase,

$(\text{CH}_3\text{NH}_3)\text{ZnPO}_4\cdot\text{H}_2\text{O}$, with an interlayer distance of 12.73 Å (Figure 3b). Similar behaviour is observed when the amines are both ethyl- and propylamine, with formation of $(\text{C}_2\text{H}_5\text{NH}_3)\text{ZnPO}_4\cdot\text{H}_2\text{O}$ and $(\text{C}_3\text{H}_7\text{NH}_3)\text{ZnPO}_4\cdot\text{H}_2\text{O}$, with basal spacings of 14.34 and 15.88 Å, respectively (see Figures 3c, d). In all three cases, combining those corresponding to both the initial and final products may reproduce the powder X-ray diffraction patterns of samples with intermediate conversion degrees. Therefore, the reaction can be represented by scheme (1), where $n = 1-3$. Although the rate of the process decreases on increasing the alkyl chain length of the amine, the reaction is completed in less than two weeks in all three cases (see Figure 6). The IR spectrum (Figure 4b) of the compound with propylamine (and also with methyl- and ethylamine) confirms the absence of ammonium groups (disappearance of the band at 1450 cm^{-1}) and the presence of protonated amino groups (1560 cm^{-1}) and structural water (1640 cm^{-1}).



The reaction of *n*-butylamine takes place with the formation of a unique phase with an interlayer distance of 17.67 Å (Figure 3e). The experimental analytical data (Table 2) indicates that this new compound is anhydrous. TG-DTG data confirms this fact. Thermal decomposition of the compound with propylamine (and also with methyl- and ethylamine) shows that the loss of crystallization water is completed at 100°C (Figure 7a), following the amine desorption process in the interval of temperatures $200-340^\circ\text{C}$. Phosphate to pyrophosphate condensation occurs later, at 440°C . However, the material with *n*-butylamine is stable below 180°C (Figure 7b). Only in subsequent heating, $180-400^\circ\text{C}$, does the loss of amine take place in two overlapping steps; condensation to pyrophosphate subsequently taking place to thus obtain $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$.

When the reaction involves *n*-butyl-, *n*-pentyl-, and *n*-hexylamine, the process is very slow. In the case of *n*-butylamine (Figure 6d), an anhydrous saturated compound is obtained after ca. 40 days, while the reaction takes months for both *n*-pentyl- (Figure 6e) and *n*-hexylamine (Figure 6f), also with formation of anhydrous phases (interlayer spacing 20.60 and 21.98 Å, respectively) that coexist with the starting material. In these cases, the reaction can be represented by scheme (2), where $n = 4-6$.



The hydration degree of the materials is a function of the characteristics of the amines. When these are methyl-, ethyl- and propylamine, the compounds have a crystallization water molecule per formula. However, compounds with larger amines are anhydrous. This fact should be explained as a consequence of the hydrophobic interaction that increases with the number of carbon atoms in the alkyl chain.

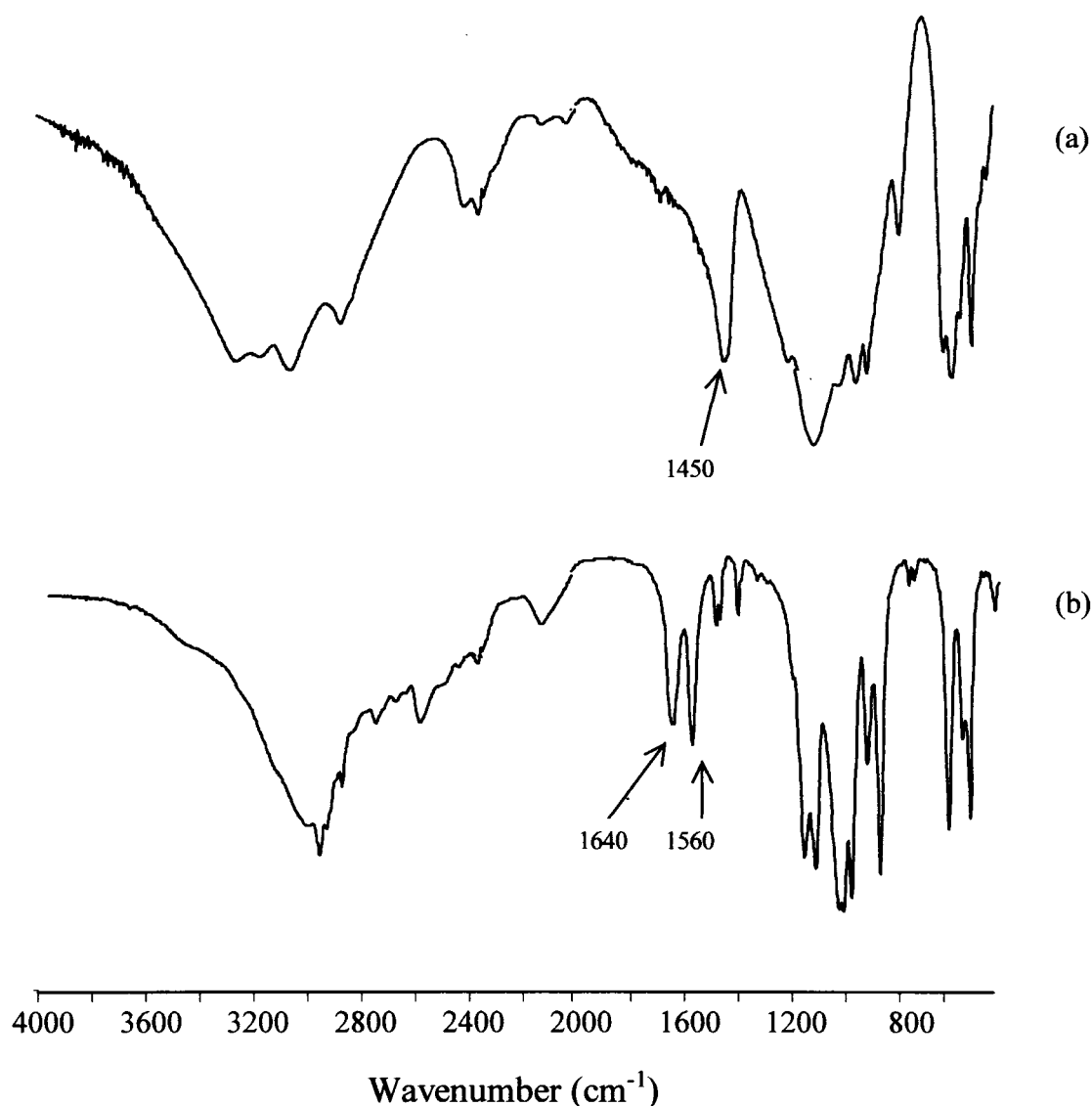


Figure 4. Infrared spectra of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ (a), and its intercalation compound with propylamine (b).

Table 1. Microanalytical data (C and N) and experimental weight loss at 1000 °C of the $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)\text{ZnPO}_4 \cdot \text{H}_2\text{O}$ ($n = 1-3$) reaction compounds

Amine	Experimental			Calculated		
	% C	% N	% w.l.	% C	% N	% w.l.
Methylamine	5.72	6.59	26.04	5.70	6.65	27.56
Ethylamine	11.62	6.53	30.49	10.69	6.24	32.08
Propylamine	16.29	5.86	34.68	15.10	5.87	36.07

Table 2. Microanalytical data (C and N) and experimental weight loss at 1000 °C of the $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)\text{ZnPO}_4$ ($n = 4-6$) reaction compounds

Amine	Experimental			Calculated		
	% C	% N	% w.l.	% C	% N	% w.l.
<i>n</i> -Butylamine	20.03	5.75	33.97	20.47	5.97	34.98
<i>n</i> -Pentylamine	24.68	5.37	39.02	24.15	5.63	38.64
<i>n</i> -Hexylamine	27.85	5.41	42.14	27.44	5.33	41.92

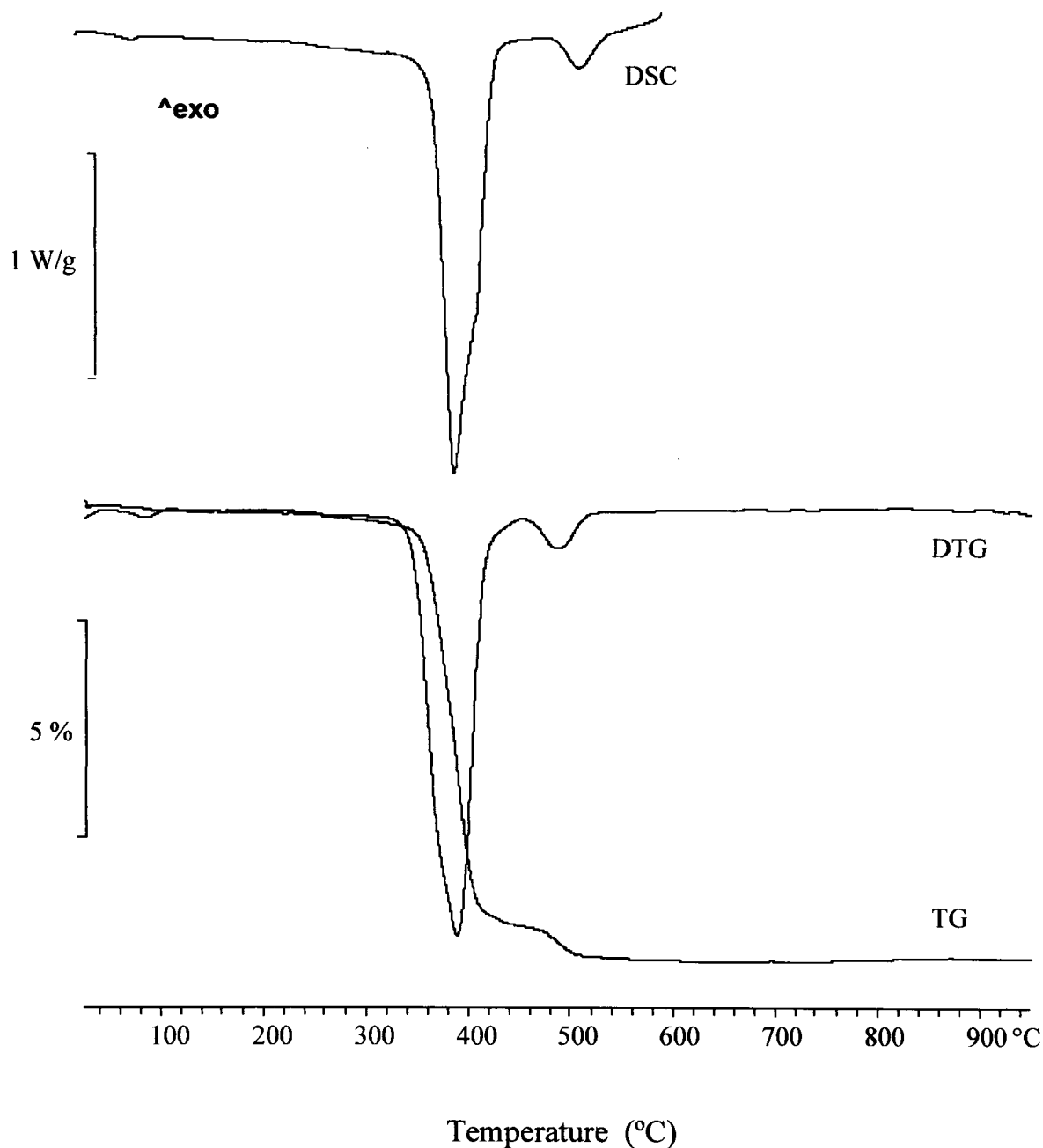


Figure 5. DSC and TG-DTG curves for $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$.

Reaction with *n*-alkylamines couples

When $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ is placed in an atmosphere saturated with both ethyl- and *n*-pentylamine (or *n*-hexylamine) vapors, reaction of the amine with a long chain occurs. The anhydrous *n*-pentylamine saturated phase (see Table II and Figure 3f) is attained in 8 days (10 days for *n*-hexylamine, Figure 3g). With less contact time, the reaction is partial, and the powder X-ray diffraction patterns detect the presence of *n*-pentylamine (or *n*-hexylamine) reaction compound and the characteristic bands to the host material. The formation of ethylamine compound is not observed, nor are any mixed compounds detected.

It is worth noting that the full reaction of *n*-pentylamine and *n*-hexylamine into $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ is not pos-

sible after 73 days to contact time (see Figure 6). However, when the process is carried out in the presence of ethylamine, the reaction time is reduced considerably. Therefore, ethylamine acts as a good catalyst in the *n*-pentylamine (or *n*-hexylamine) sorption.

Reaction with *n*-alkylamines mixtures

When $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ is placed in contact with a mixture of vapors of *n*-alkylamines ($n = 1-6$), the composition of the compounds obtained is greatly dependent on the reaction time. After 12 hours, the powder X-ray diffraction shows the signals of the starting material and a phase with 17.67 Å interlayer distance, which corresponds to the sorption of *n*-butylamine. After 80 hours, the

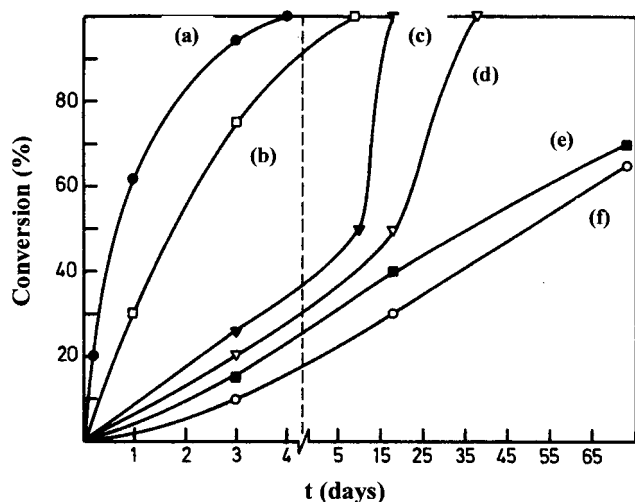


Figure 6. Conversion degree versus contact time for the reaction of methyl- (a), ethyl- (b), propyl- (c), *n*-butyl- (d), *n*-pentyl- (e), and *n*-hexylamine (f).

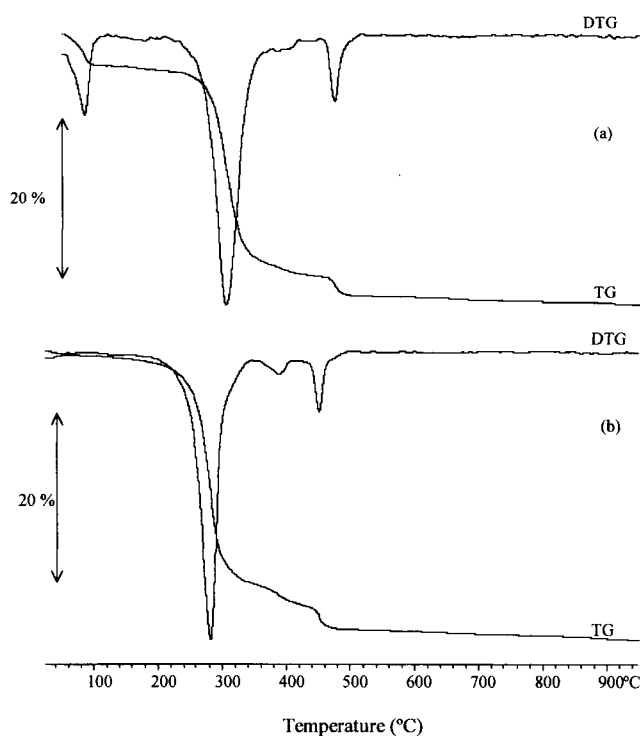


Figure 7. TG-DTG curves of the phases with propyl- (a) and *n*-butylamine (b).

process provides the unique uptake of *n*-pentylamine (experimental C/N molar ratio = 5.01). At a longer contact time, *n*-pentylamine is replaced by *n*-hexylamine, until the pure *n*-hexylamine compound is attained (ca. 200 hours, experimental C/N molar ratio = 6.05).

Arrangement of the amines in the solid phase

Powder X-ray diffraction data for $(\text{CH}_3\text{NH}_3)\text{ZnPO}_4 \cdot \text{H}_2\text{O}$ are shown in Table 3. The pattern was indexed on a triclinic unit cell: $a = 5.505(4)\text{Å}$, $b = 9.093(3)\text{Å}$, $c = 12.854(6)\text{Å}$, $\alpha = 86.01(2)^\circ$, $\beta = 89.43(1)^\circ$, $\gamma = 80.91(2)^\circ$. This unit cell is close to the $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ [$a = 5.2442(5)\text{Å}$, $b = 8.938(2)\text{Å}$, $c = 9.731(2)\text{Å}$, $\alpha =$

Table 3. Powder XRD data for $(\text{CH}_3\text{NH}_3)\text{ZnPO}_4 \cdot \text{H}_2\text{O}$

h	k	l	d_{calc} (Å)	d_{obs} (Å)	I/I ₀
0	0	1	12.800	12.801	100
0	1	0	8.955	8.917	5
0	-1	1	7.603	7.623	4
0	0	2	6.410	6.419	16
1	0	1	4.966	4.973	2
1	-1	1	4.702	4.686	3
0	2	0	4.478	4.476	7
1	1	0	4.349	4.360	2
0	-1	3	3.969	3.959	4
1	-2	1	3.655	3.654	2
1	1	2	3.515	3.497	11
-1	0	3	3.394	3.395	2
1	0	3	3.325	3.326	3
1	2	0	3.214	3.217	2
0	0	4	3.205	3.209	1
-1	2	1	3.166	3.162	2
-1	-1	3	3.131	3.129	7
1	2	1	3.071	3.071	8
1	2	2	2.802	2.814	5
2	-1	1	2.664	2.670	3
2	0	1	2.647	2.652	10
0	0	5	2.564	2.565	1
0	-3	3	2.534	2.535	5
2	0	2	2.483	2.483	5
1	-3	3	2.413	2.408	1
2	-2	2	2.351	2.351	3
2	1	2	2.293	2.290	3
1	3	2	2.243	2.244	1
2	2	0	2.175	2.178	2
2	-2	4	1.995	1.996	5

$75.01(2)^\circ$, $\beta = 77.72(2)^\circ$, $\gamma = 73.06(1)^\circ$] [40], suggesting that the methylamine sorption does not substantially modify the structure of the layers. Although the index has only been possible for this compound, the characteristics of the X-ray diffraction patterns for the other *n*-alkylamine compounds (see Figure 3) indicates that this behavior is general for all materials. Figure 8 shows the interlayer distances of the sorption compounds of the *n*-alkylamines into $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ against the number of the carbon atoms of the amine. The straight line defines Equation (3), where n_c is the number of carbon atoms in the alkyl chain. Since the increment in the alkyl chain length, in the *trans-trans* conformation, is estimated to be 1.27Å for each additional carbon atom [47], it is reasonable to assume that the amines are present in the $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ as a bimolecular layer of extended molecules with their longitudinal axis inclined at an average of 48.4° ($\sin^{-1}[1.90/(2 \times 1.27)]$) with respect to the plane of the sheet.

$$d = 10.51 + 1.90 n_c \quad (3)$$

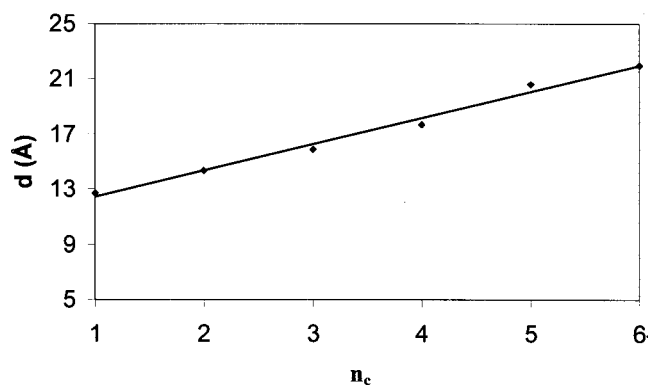


Figure 8. Interlayer distance of reaction compounds of $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ with n -alkylamines as a function of the number of carbon atoms in the alkyl chain, n_c .

The interlayer distance of all phases (both, monohydrated and anhydrous) define a unique straight line, indicating that the water molecule does not appreciably affect the value of solid basal spacing. Although this fact is not very frequent, precedents exist in this sense [38]. Usually, the compounds that present this behavior possess a relatively low packing density for the organic species. In the materials synthesized in this work, the amines only recover ca. 79% of the sheet surface. This data is obtained from the ratio between the cross sectional area of a *trans-trans* alkyl chain, evaluated in 18.6 \AA^2 [48], and the free area surrounding each hydrogenphosphate group in $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$, 46.9 \AA^2 , which permits the accommodation of two molecules of n -alkylamine, one of them associated to the HPO_4 group and another substituting to the ammonia position. The water molecules can occupy the empty spaces without appreciable change of the interlayer distance, that is defined by both the length and the orientation of the alkylchains.

The reaction of the n -alkylamines with $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ is a complex process that involves two chemically different active centers: the hydrogen of the HPO_4 groups and the ammonium ions. Moreover, by thermal treatment, is not possible to obtain the initial ammonium phase since that the final materials no longer contain ammonia. In this way, thermal treatment at 250°C of methylamine compound originates a layered solid (Figure 9) with $(\text{CH}_3\text{NH}_3)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ composition (experimental analytical data: 4.05% N and 3.46% C; calcd.: 3.98% N and 3.41% C). Both the reverse of process and the nonexistence of strong chemical bonds between guest and host are two fundamental demands that should satisfy a process to take the intercalation name.

Conclusions

The reaction of n -alkylamines with $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ layers provides materials with the composition $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)\text{Zn}_2\text{PO}_4 \cdot x\text{H}_2\text{O}$ ($n = 1-3$, $x = 1$; $n = 4-6$, $x = 0$). The amine molecules are placed in the interlayer region in a bilaminar arrangement with their alkyl chain

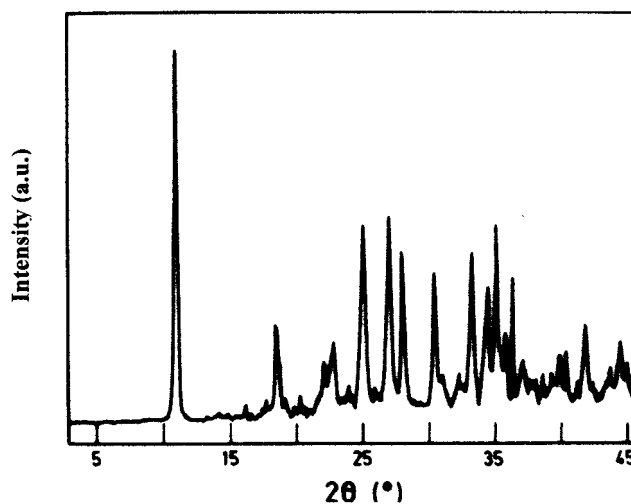


Figure 9. Powder X-ray diffraction pattern of $(\text{CH}_3\text{NH}_3)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$.

tilted at an angle of 48.4° to the phosphate layer. In complex systems, the final product of the reaction between $(\text{NH}_4)\text{Zn}_2(\text{PO}_4)(\text{HPO}_4)$ and n -alkylamine mixed vapors is a function of the contact time. The thermodynamic stability of the reaction product increases with the length of the alkyl chain of the amine. Therefore, a long reaction time is necessary to reach equilibrium conditions and is very sensitive to the amine mixture.

Acknowledgements

We gratefully acknowledge the financial support for this study from the *Ministerio de Ciencia y Tecnología* (Spain), and the *Consejería de Educación y Cultura* (Principado de Asturias): Research Projects Nos. MAT2000-1654 and PR-01-GE-4.

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