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Thermal behaviour of α-titanium phosphate/ *n*-alkylamine intercalation compounds

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Abstract

The thermal decomposition of the intercalation compounds α-Ti$(OPO_3)_2 \cdot 2C_nH_{2n+1}NH_3 \cdot H_2O$ ($n = 1$–6) is studied. Decomposition takes place in seven steps. The crystallization water is lost in the first step and the condensation of the hydrogenphosphate groups into pyrophosphate takes place in the last step. In the remaining five steps, the intercalated amine is desorbed, the last product being TiP_2O_7 in every case. Materials of formula $TiH_{2-y}(OPO_3)_2 \cdot yC_nH_{2n+1}NH_3$ ($y = 2.0$, 1.7, 1.3, 1.0) have been characterized. When $y = 2.0$, 1.7 or 1.3 the *n*-alkylamines form a bimolecular film. The interlayer distance of the intercalates decreases with decreasing amine content of the solids. Likewise, the inclination angle of the alkyl chains with respect to the phosphate layer decreases. When $y = 1.0$ the *n*-alkylamines form a monomolecular film.

INTRODUCTION

Special attention has been paid to the lamellar phosphates of tetravelent metals as ionic exchangers, catalysts and catalyst supports. Amongst them, should be noted the α and γ varieties of the titanium and zirconium phosphates [1–5]. In addition to their lamellar structure several phosphates present a high degree or crystallinity; they are resistant to degradation and adequate for use under a variety of conditions [5].

The possibility of these materials intercalating organic molecules in their interlayer spaces [5–8] with formation of compounds with moderate thermal stability [9, 10] is well known. The ionic substitution processes as well as the insertion of organic molecules give rise to the expansion (or sometimes the contraction) of the interlayer distance of the system [5].

Many studies have been carried out concerning the intercalation of the *n*-alkylamines in compounds such as α-ZrP [11, 12], α-SnP [13, 14] and α-TiP [15] where α-MP stands for α-M$(HPO_4)_2 \cdot H_2O$. Nevertheless, the study of the thermal behaviour of these materials has not been well developed. This paper studies the thermal behaviour of the intercalation compounds α-TiP/*n*-alkylamine.

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EXPERIMENTAL

All chemicals used were of reagent grade. α-TiP was prepared following the method of Alberti et al. [16], using 10 M H_3PO_4 and a reflux time of 50 h. Intercalation compounds with *n*-alkylamines were obtained by placing the α-TiP in an atmosphere saturated with *n*-alkylamine vapour at room temperature [15]. The intercalated samples were air dried at 50°C and stored in a desiccator over a solution of 50% H_2SO_4.

The analysis of the concentration of phosphorus and titanium in the solids was carried out gravimetrically. Microanalytical data (C, H and N) were obtained with a Perkin-Elmer Model 240B elemental analyser. Thermal analysis was performed by a Mettler Model TA4000 (TG50, DSC30; atmosphere of nitrogen; rate of heating 5°C min^{-1}). The diffractometer used was a Philips Model 1050/23 ($\lambda = 1.5418$ Å).

RESULTS AND DISCUSSION

In an earlier paper [15] the synthesis of intercalation compounds α-TiP/*n*-alkylamine was described. In all cases, the intercalation involves every active centres of the solids; namely two moles of amine per mole of α-TiP are intercalated giving rise to compounds with the formula α-$Ti(OPO_3)_2 \cdot 2RNH_3 \cdot H_2O$. The intercalation takes place with formation of a double layer of amine molecules in trans–trans conformation. The inclination of the bimolecular layer of amine is 58.7° with respect to the basal plane of α-TiP. The packing parameters obtained for these solids have values near to unity (except for the methylamine complex) indicating that the packing density of the amine in the interlayer space is very close to that of the *n*-paraffin crystals. The value of the packing parameter obtained for the methylamine complex (0.73) explains the capacity of this compound to take up additional amounts of methylamine.

Table 1 shows the mass losses of the α-TiP/*n*-alkylamine intercalation compounds when they are treated from room temperature to 800°C. They

TABLE 1

Experimental mass loss (%) of the intercalation compounds at 800°C and that calculated from the α-$Ti(OPO_3)_2 \cdot 2RNH_3 \cdot H_2O$ formula

Amine	Experimental	Calculated
Methylamine	30–40	30.6
Ethylamine	36.2	36.2
Propylamine	39.9	40.9
Butylamine	46.5	45.1
Pentylamine	46.8	48.6
Hexylamine	53.2	51.8

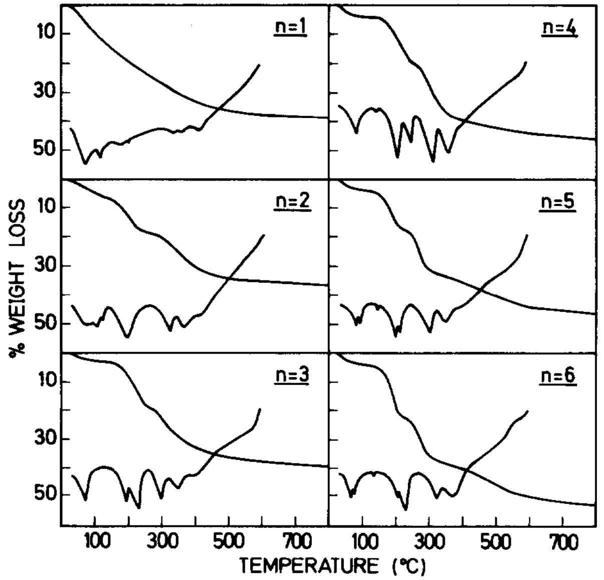

Fig. 1. TG and DSC curves of the α-Ti(OPO$_3$)$_2$ · 2C$_n$H$_{2n+1}$NH$_3$ · mH$_2$O ($n = 1$–6) compounds.

are compared to those calculated by supposing the existence of one molecule of water of crystallization per formula. The agreement is good except in the case of the α-TiP/methylamine compounds where the experimental loss of mass depends on the contact time between the α-TiP and the methylamine. This behaviour is foreseeable because when methylamine is intercalated a lamellar crystalline material with a definite structure is obtained after a few contact hours, but if the solid stays in the amine vapour atmosphere it transforms into an amorphous gel and the percentage of amine in solid phase increases [15]. In Fig. 1 the TG and DSC curves of these compounds are shown. The samples were treated from room temperature to 800°C in the TG analysis, but only to 600°C in the DSC.

When the intercalated amine is methylamine, the TG curves show that the loss of mass takes place in a continuous way and it is impossible to detect temperature zones where a stable compound is obtained. Nevertheless, DTG shows that the process rate is not constant, and relative maxima in the rate of the mass loss at 65, 110, 190, 330 and 420°C are detected. The DSC curve shows two minima at 70 and 115°C, followed by additional, less well defined, endothermic processes at the temperatures shown in Table 2. The elemental analysis for the sample and its total loss of mass lead us to propose the formula $Ti(OPO_3)_2 \cdot 2CH_3NH_3 \cdot 0.5CH_3NH_2 \cdot 2H_2O$ for this compound.

TG curves of the remaining intercalation compounds show comparable shapes. The existence of at least three well defined processes of mass loss

TABLE 2

Temperatures (°C) corresponding to the DSC peaks of the α-$Ti(OPO_3)_2 \cdot 2RNH_3 \cdot mH_2O$ intercalation compounds

Amine	A	B	C	D	E	F	G
Methylamine	70	115	180	—	340	365	>415
Ethylamine	75.95	120	195	—	320	365	>415
Propylamine	70	—	195	230	300	350	>460
Butylamine	80	150	205	245	335	360	>490
Pentylamine	80.90	140	195	215	305	350	>550
Hexylamine	60.75	135	200	230	320	370	>560

can be observed. The first takes place at temperatures lower than 100°C and corresponds to the loss of water of crystallization. In a second step, the anhydrous compounds at temperatures lower than 250°C lose an amount of *n*-alkylamine corresponding to one molecule per formula. Finally, at temperatures higher than 300°C, a new step is observed corresponding to the loss of the second molecule of *n*-alkylamine and to the water of crystallization (transformation of the hydrogenophosphate groups into pyrophosphate). DTG and DSC curves show that the thermal desorption process is more complicated since six to seven bands are observed in every sample, indicating the presence of at least the same number of steps for the decomposition process. The temperatures of the bands characteristic of the DSC curves are compiled in Table 2. These temperatures can be grouped into seven blocks A–G, suggesting unique behaviour in the thermal decomposition of the α-TiP/*n*-alkylamine intercalation compounds. From these data, a sequence of loss of mass for all the intercalation compounds is proposed

$$\begin{aligned}&Ti(OPO_3)_2 \cdot 2RNH_3 \cdot H_2O \xrightarrow{A} Ti(OPO_3)_2 \cdot 2RNH_3 \xrightarrow{B}\\ &\quad TiH_{0.3}(OPO_3)_2 \cdot 1.7RNH_3 \xrightarrow{C} TiH_{0.7}(OPO_3)_2 \cdot 1.3RNH_3 \xrightarrow{D}\\ &\quad TiH(OPO_3)_2 \cdot RNH_3 \xrightarrow{E} TiH_{1.5}(OPO_3)_2 \cdot 0.5RNH_3 \xrightarrow{F}\\ &\quad Ti(HOPO_3)_2 \xrightarrow{G} TiP_2O_7 \qquad (1)\end{aligned}$$

Monohydrated compounds lose their water of crystallization at temperatures between 60 and 95°C (A), the existence of wide bands being observed in DSC curves at these temperatures which sometimes split in two narrower bands indicating that the process would take place in two steps, which are usually difficult to distinguish. At temperatures between 100 and 250°C half of the intercalated *n*-alkylamine molecules are lost.

The process takes place in three steps corresponding to 115–150°C (B), 180–205°C (C) and 215–245°C (D). TG and DSC data are consistent with the hypothesis that in every step a third of the *n*-alkylamine lost between 100–250°C is desorbed. At temperatures from 300 to 400°C the rest of the intercalated *n*-alkylamine is lost. The process takes place in two steps at 300–340°C (E) and 350–370°C (F) the mass lost being the same in both steps. Therefore, at 400°C a material with the formula $Ti(HPO_4)_2$ is obtained regardless of the nature of the initial compound. A similar material is also obtained when α-TiP is treated to give lamellar compounds with a basal spacing of 7.4 Å. The condensation of the hydrogenphosphate groups into TiP_2O_7 in α-TiP takes place in a narrow range of temperatures at about 520°C. DSC curves of the intercalation compounds indicate that, in these cases, the formation of titanium pyrophosphate does not take place at a defined temperature but bands of low intensity are detected over a wide temperature range. Table 2 shows temperatures at which the loss of water of crystallization commences. These temperatures increase as the length of the alkyl chain in the amine increases. The lack of well defined bands corresponding to this process should be related to the low crystallinity of the anhydrous TiP obtained.

Once the thermal desortion sequence and the different step temperatures were known, we tried to isolate intermediate pure phases. Thus, masses of about 1 g of every intercalation compound were treated at 80, 130, 190, 240, 300, 360, 550 and 1000°C during 3 h. X-Ray patterns of the samples obtained indicate that pure phases are not isolated in most cases.

In order to explain this behaviour a thermogravimetric programme was designed based upon heating at constant rate (20°C min^{-1}) of the α-TiP/*n*-alkylamine samples from room temperature to the different temperatures chosen. Once the desired temperature was reached, the sample was maintained at constant temperature during 3 h. The mass variation is known throughout the entire process. The results obtained are shown in Figure 2.

It can be observed that except in the α-TiP/methylamine compound, the total loss of mass during the dynamic-isothermal treatment concurs with that expected for compounds with the formula $Ti(OPO_3)_2 \cdot 2RNH_3 \cdot H_2O$. When RNH_2 is methylamine the loss of mass is higher, as previously discussed. In the cases of compounds with a defined composition, a constant mass is obtained only when treatment temperatures are 80, 130, 190 and 550°C, but not in all compounds. In α-TiP/methylamine, the loss of mass is a continuous process which finishes with formation of TiP_2O_7. When the intercalated amine is ethylamine constant mass is attained when the treatment temperatures are 80 and 190°C. At 80°C, the loss of mass corresponds to that expected for process A in scheme (1). At 190°C the $TiH(OPO_3)_2 \cdot C_2H_5NH_3$ compound is stabilized. With regard to propyl-, butyl-, pentyl- and hexylamine, anhydrous intercalation com-

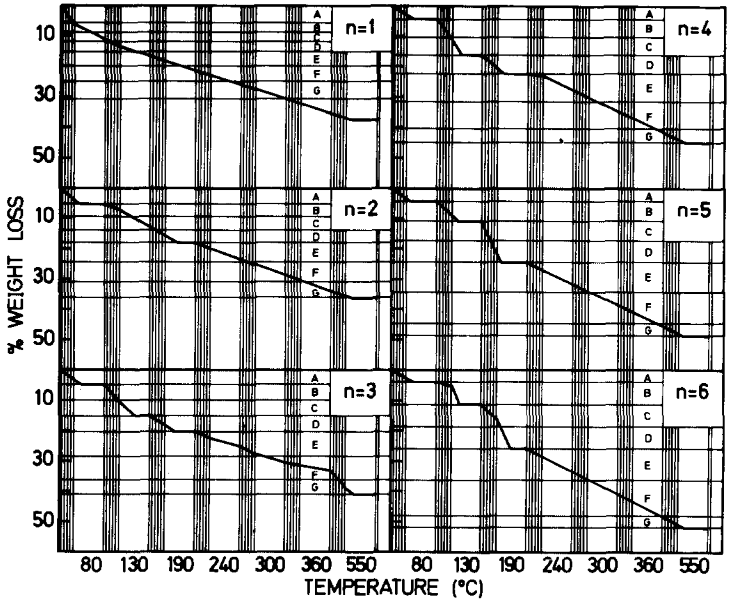

Fig. 2. Dynamic-isothermal TG curves of the α-$Ti(OPO_3)_2 \cdot 2C_nH_{2n+1}NH_3 \cdot mH_2O$ (n = 1–6) compounds. In the non-dashed zone, the temperature remains constant and equal to the corresponding abscissa value. In the zone between two constant temperatures (vertical lines) the rate of heating is 20°C min^{-1}. The horizontal lines correspond to the theoretical loss of mass if the process of eqn. (1) takes place.

pounds are also obtained at 80°C while at 190°C the compounds obtained have the formula $TiH(OPO_3)_2 \cdot RNH_3$. Moreover, constant mass is obtained at 130°C, the compounds $TiH_{0.7}(OPO_3)_2 \cdot 1.3RNH_3$ (R = propyl, butyl) and $TiH_{0.3}(OPO_3)_2 \cdot 1.7RNH_3$ (R = pentyl, hexyl) being obtained.

X-ray patterns of the samples treated at 80, 130, 190, 240, 300, 500 and 1000°C give additional information. When α-TiP/methylamine is treated at 80°C, a well defined reflection at 8.8 Å and a wide band of 10–11 Å are observed. This pattern is similar to that obtained when the treatment temperatures are 130 and 190°C. At 240°C, a new reflection at 7.8 Å is detected coexisting with additional reflections at 8.8 and 7.4 Å, this latter corresponding to the anhydrous α-TiP. The reflection at 7.4 Å is the only one observed at 300°C. The patterns of the samples treated at 360 and 550°C are characteristic of the amorphous material.

When α-TiP/ethylamine is treated at 80°C the interlayer distance of the material is almost the same that in the initial compound (14.3 Å). At 130°C two bands at 12.0 and 10.8 Å coexist, this latter remaining at 190°C. The composition of this compound is $TiH(OPO_3)_2 \cdot C_2H_5NH_3$. At 240°C this phase coexists with anhydrous α-TiP (d_{002} = 7.4 Å). The reflection at 7.4 Å is the only one observed at 300 and 360°C. The crystallinity of the material obtained at 550°C is low although lamellar traces are still present (d_{002} = 6.8 Å).

The treatment of α-TiP/propylamine at 80°C initiates dehydration but the interlayer distance (16.9 Å) is not noticeably modified. This distance decreases to 14.6 Å when the treatment temperature is 130°C. The composition of this compound is $TiH_{0.7}(OPO_3)_2 \cdot 1.3C_3H_7NH_3$. At 190°C, the $TiH(OPO_3)_2 \cdot C_3H_7NH_3$ phase is obtained with $d_{002} = 11.7$ Å. At 240°C, a wide band at 11 Å is detected coexisting with the anhydrous α-TiP. At temperatures higher than 300°C the behaviour is similar to that described for α-TiP/ethylamine.

The interlayer distance of α-TiP/butylamine does not vary upon thermal treatment at 80°C (18.8 Å). At 130°C $TiH_{0.7}(OPO_3)_2 \cdot 1.3C_4H_9NH_3$ is obtained with an interlayer distance of 16.5 Å. At 190°C the loss of one amine molecule is complete with formation of $TiH(OPO_3)_2 \cdot C_4H_9NH_3$ ($d_{002} = 12.4$ Å). At 240°C a wide band at 10 Å coexisting with that of anhydrous α-TiP is detected. The behaviour at temperatures higher than 300°C is similar to that described for α-TiP/ethylamine.

At 80°C, anhydrous α-TiP/pentylamine maintains its initial interlayer distance (21.1 Å). Nevertheless, at 130°C this decreases to 20.2 Å and $TiH_{0.3}(OPO_3)_2 \cdot 1.7C_5H_{11}NH_3$ is formed. At 190°C the $TiH(OPO_3)_2 \cdot C_5H_{11}NH_3$ phase ($d_{002} = 14.7$) is obtained. At 240°C, a wide band at 13 Å coexisting with anhydrous α-TiP is detected. The reflection at 7.4 Å is the only one observed at 300°C. The patterns of the sample treated at 360 and 550°C are characteristic of amorphous materials.

The dehydration of α-TiP/hexylamine at 80°C does not noticeably modify its interlayer distance of 23.1 Å. Treatment at 130°C causes it to decrease to 21.7 Å, corresponding to $TiH_{0.3}(OPO_3)_2 \cdot 1.7C_6H_{13}NH_3$. At 190°C the $TiH(OPO_3)_2 \cdot C_6H_{13}NH_3$ phase is stabilized ($d_{002} = 15.5$ Å). At 240°C, two bands at 7.4 Å (anhydrous α-TiP) and 13 Å are observed. At 300°C this latter distance moves to higher angles reaching values near to 11.5 Å. The patterns obtained by treatment at 360 and 550°C are characteristic of amorphous materials.

In every case treatment at 1000°C causes titanium pyrophosphate to crystallize.

Table 3 shows the interlayer distances of the crystalline phases isolated during thermal decomposition of the α-TiP/n-alkylamine compounds. The results of plotting these distances against the number of carbon atoms in the amine alkyl chain can be seen in Fig. 3. Materials with the same amine content define straight lines with the expressions (2)–(5).

$$Ti(OPO_3)_2 \cdot 2RNH_3 \qquad d_{002} = 10.1 + 2.17n_C \tag{2}$$

$$TiH_{0.3}(OPO_3)_2 \cdot 1.7RNH_3 \qquad d_{002} = 10.1 + 1.97n_C \tag{3}$$

$$TiH_{0.7}(OPO_3)_2 \cdot 1.3RNH_3 \qquad d_{002} = 10.1 + 1.57n_C \tag{4}$$

$$TiH(OPO_3)_2 \cdot RNH_3 \qquad d_{002} = 8.3 + 1.19n_C \tag{5}$$

TABLE 3

Interlayer distances d_{002} (Å), monolaminar (M) or bilaminar disposition (B) of the alkyl ch average inclination angle α (deg) with respect to the plane of the sheet and packing parame (V_p) for the α-TiP/n-alkylamine intercalation compounds

Formula	Intercalated amine	d_{002}	Disposition	α	V_p
$Ti(OPO_3)_2 \cdot 2RNH_3$	Ethylamine	14.3	B	58.7	1.04
	Propylamine	16.9	B	58.7	0.96
	Butylamine	18.8	B	58.7	1.01
	Pentylamine	21.1	B	58.7	0.99
	Hexylamine	23.1	B	58.7	1.01
$TiH_{0.3}(OPO_3)_2 \cdot 1.7RNH_3$	Pentylamine	20.2	B	50.9	0.90
	Hexylamine	21.7	B	50.9	0.94
$TiH_{0.7}(OPO_3)_2 \cdot 1.3RNH_3$	Propylamine	14.6	B	38.2	0.97
	Butylamine	16.5	B	38.2	0.91
$TiH(OPO_3)_2 \cdot RNH_3$	Ethylamine	10.8	M	69.4	0.87
	Propylamine	11.7	M	69.4	0.96
	Butylamine	12.4	M	69.4	1.06
	Pentylamine	14.7	M	69.4	0.85
	Hexylamine	15.5	M	69.4	0.91

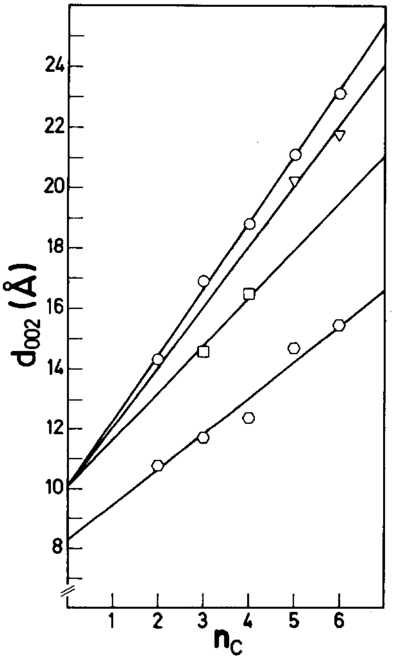

Fig. 3. Interlayer distance (d_{002}) of intercalation compounds of α-TiP with n-alkylamines as a function of the number of carbon atoms in the alkyl chain (n_C): $Ti(OPO_3)_2 \cdot 2RNH_3$, ○; $TiH_{0.3}(OPO_3)_2 \cdot 1.7RNH_3$, ▽; $TiH_{0.7}(OPO_3)_2 \cdot 1.3RNH_3$, □; $TiH(OPO_3)_2 \cdot RNH_3$, ○.

Since the increment of the alkyl chain, in the trans–trans conformation, is estimated to be 1.27 Å for each additional carbon atom [16], it is reasonable to assume that the amines are present in α-TiP as a bimolecular layer of extended molecules when the slope of the straight line defining the interlayer distances of materials with the same amine content is higher than 1.27 Å. When the value is lower than 1.27 Å the arrangement should be monolamellar. As expected in the $TiH_{2-y}(OPO_3)_2 \cdot yRNH_3$ ($y > 1$) compounds the amines are present as a bimolecular layer. However in the $TiH(OPO_3)_2 \cdot RNH_3$ materials the amines are placed in a monomolecular layer. In Table 3 are compiled the average inclination angles of the n-alkylamine molecules with respect to the titanium phosphate layer for each composition.

The packing of the alkyl chains may be expressed by the parameter $V_p = V_c/V_t$, were V_c is the volume occupied by the alkyl chains and V_t is the volume available to them in the interlayer space. V_t can be calculated by subtracting from the interlayer spacing the thickness (d') of the region occupied by the α-layer and terminal $-NH_3^+$ groups. Referred to 1 cm^2 of layer, V_t will be given by the expression (6) where d_{002} and d' are expressed in cm and V_t in cm^3.

$$V_t = d_{002} - d' \qquad (6)$$

Assuming that the interpenetration of the $-NH_3^+$ groups within the layer surface is independent of n_C, d' is equal to the value of d_{002} for $n_C = 0$. Namely, $d' = 10.1 \times 10^{-8}$ cm for a bimolecular layer of amines, and $d' = 8.3 \times 10^{-8}$ cm for a monomolecular layer. V_c for a compound of formula $TiH_{2-y}(OPO_3)_2 \cdot yRNH_3$, referred to 1 cm^2 of α-TiP layer, is

$$V_c = yn_C(1.27 \times 10^{-8})(18.6 \times 10^{-16})(4.63 \times 10^{14})\ \text{cm}^3 \qquad (7)$$

where $n_C(1.27 \times 10^{-8})(18.6 \times 10^{-16})$ cm^3 is the volume of an alkyl chain containing n_C carbon atoms deduced from the cell dimensions of crystalline $C_{29}H_{60}$ [16] and 4.63×10^{14} is the number of formula units per cm^2 of α-TiP layer calculated from the dimensions of the unit cell of the hydrogen form of the crystal [17].

The values of the packing parameter for the α-materials are shown in Table 3. It can be seen that V_p always takes values higher than 0.85, indicating that the packing density is not very different to that present in the crystalline n-paraffin. Namely, the arrangement of the n-alkylamines in the interlayer region agrees with the "space filling" postulate [18], predicting that the most probable arrangement should be that in which the most economical use is made of the interlayer space.

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