

# Intercalation of Diamines into Zirconium Phosphate-Phosphite: A Layered Compound with Asymmetric Layers

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**Abstract.** Many primary diamines  $H_2N(CH_2)_nNH_2$  (all the members with  $n$  ranging from 0 to 12 with the exception of  $n = 11$ ) have been intercalated within the phosphate regions of layered zirconium phosphate-phosphite. As a general rule, intercalation occurs in two steps that are not well differentiated. The first one leads to intercalation compounds in which the diamines are arranged with their alkyl chain oriented parallel to the layers; the second one to the fully intercalated compounds. These latter compounds have composition  $Zr(HPO_4)_{0.7}(HPO_3)_{1.3} \cdot \gamma NH_2(CH_2)_n \cdot NH_2$ , with  $\gamma$  ranging from 0.36 to 0.49 depending on the nature of the diamine. Not all the diamine molecules are thus diprotonated and they show a tendency to reach a  $\gamma$  value of 0.5, corresponding to the total occupancy of the crystal sites available for intercalation. Diamines are arranged as a monolayer of extended molecules and an evident even-odd alternation of the interplanar spacing has been observed.

A comparison with the intercalation of  $\alpha$ -zirconium phosphate for the same diamines is also made.

**Key words.** zirconium phosphate phosphite, asymmetric layered compound,  $\alpha$ ,  $\omega$ -alkyldiamines, hydrazine, even-odd effect.

## 1. Introduction

Zirconium phosphate-phosphite may be considered as the prototype of a new class of layered compounds of general formula  $Zr(RPO_3)_x(R'PO_3)_{2-x}$  where R and R' are inorganic or organic radicals [1]. These compounds, also known as derivatives of  $\alpha$ -zirconium phosphate with two different pendant groups, have kindled interest in the field of ion exchange, intercalation and heterogeneous catalysis, because their reactivity may be modulated by the suitable choice of R and R' moieties [2, 3]. Moreover, some of them exhibit interesting structures built up of chemically asymmetric layers. This is the case for zirconium phosphate-phosphite (R = OH, R' = H,  $x = 0.7$ ).

Due to its peculiar structure [4], the ion exchange and intercalation properties of zirconium phosphate phosphite (ZrPP) were found to be different from those of the parent compound,  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (ZrP). In previous papers, the ion exchange of alkali metal ions [5] and the intercalation of alkylmonoamines [6] in ZrPP have been discussed. The present paper reports an investigation on the intercalation of  $\alpha$ ,  $\omega$ -alkyldiamines. Hydrazine was also studied.

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## 2. Experimental

### 2.1. MATERIALS

ZrOCl<sub>2</sub>·8 H<sub>2</sub>O was a Merck 'pro analysi' product. Diamines were supplied by Fluka and all other reagents were from C. Erba, R.P.E. grade. Microcrystals of ZrPP, having the composition Zr(HPO<sub>4</sub>)<sub>0.7</sub>(HPO<sub>3</sub>)<sub>1.3</sub>·0.5 H<sub>2</sub>O were prepared according to the HF procedure [1] (100 mL of an aqueous solution 1.2 M in ZrOCl<sub>2</sub> and 7.2 M in HF were added to 900 mL of a solution 4.1 M in H<sub>3</sub>PO<sub>4</sub> and 1.1 M in H<sub>3</sub>PO<sub>3</sub>; the resulting clear solution was heated at 80°C in a water bath for four days. Distilled water was added periodically to keep the volume constant). The microcrystals obtained were washed with distilled water until the washing solutions reached pH 4 and dried at ambient temperature and 75% relative humidity; their size, evaluated from a SEM micrograph, ranged between 5–40 μm.

### 2.2. INTERCALATION PROCEDURE AND APPARATUS

The intercalation reactions were achieved by titrating the host with standardized diamine solutions at room temperature. Direct titration curves were obtained with a Mettler DK automatic titrimeter operating in the equilibrium point mode. A 0.05M diamine solution was added stepwise to 0.500 g of ZrPP, suspended in 40 mL of 0.05M diamine hydrochloride solution; each addition was of 0.01 mL when the change in pH was less than 0.03 pH unit min<sup>-1</sup>. In some cases, in order to follow the phase transitions occurring at various degrees of intercalation by X-ray diffractometry, the titration curves were also determined by the batch procedure [7].

Samples of fully intercalated ZrPP with the various diamines were also prepared by equilibrating 1 g of ZrPP with an excess of diamine solutions (100 mL 0.050M) for four days. X-ray analysis was performed on both wet and dried (at ambient temperature and 75% of relative humidity) samples by means of a computer controlled Philips diffractometer, using Ni filtered CuK<sub>α</sub> radiation. The step scanning procedure (step size 0.03°) was used. Side loaded samples were analyzed to minimize preferred orientation effects.

The water content of the intercalates was determined by TG measurements performed on a Stanton STA 781 Thermoanalyzer at the heating rate of 5°C/min, in an air flow. The amount of the diamines intercalated was derived from H, C, N elemental analysis (C. Erba Model 1106 Analyzer) of the intercalates.

The diamine intercalation *vs* time curves were obtained with a Mettler DK automatic titrimeter operating in the pHstat mode. The titrimeter records, as a function of time, the volume of 0.050M diamine solution necessary to maintain at 7 the pH of a slurry of 0.500 g of host dispersed in 40 mL of 0.050M amine hydrochloride, held at 20°C under constant stirring.

## 3. Results and Discussion

Before discussing the experimental results of the present investigation it is useful to briefly recall the layered structure of ZrPP determined from X-ray powder data [4].

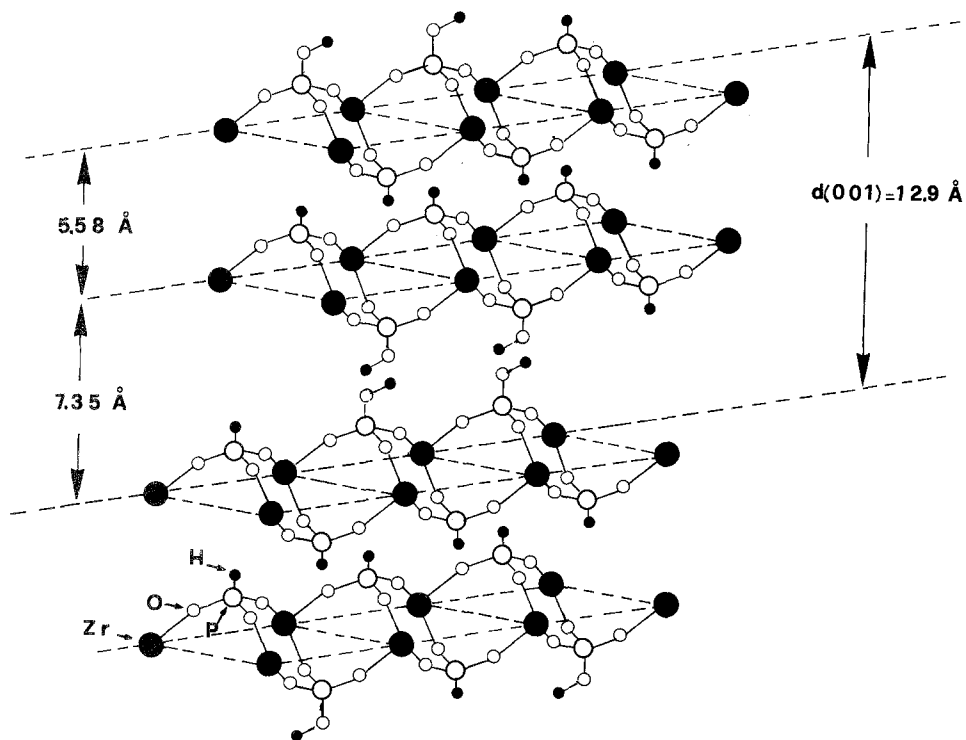


Fig. 1. Schematic view of the packing of asymmetrical layers in the layered structure of zirconium phosphate phosphite.

As illustrated in Figure 1 the stacking of the  $\alpha$ -layers, containing phosphite groups on one side and an excess of phosphate groups on the other, occurs in such a way that an interlayer region of zirconium phosphate type regularly alternates with one of zirconium phosphite. The repeat distance along the stacking direction, corresponding to the interplanar spacing of 001 reflections,  $d(001) = 12.9 \text{ \AA}$ , is very close to the sum of the interlayer distances typical of  $\alpha$ -zirconium phosphate containing some phosphite groups ( $d_1 = 7.4 \text{ \AA}$ ) [4] and of that of  $\alpha$ -zirconium phosphite ( $d_2 = 5.6 \text{ \AA}$ ) [4, 8], respectively.

Only the phosphate groups are involved in ion exchange and intercalation processes, the hydrogen of the phosphite groups having a non acidic character. As a consequence, only the phosphate regions expand to accommodate the guest species.

Accordingly, the expansion can be monitored by evaluating  $d_1$  through the simple equation:

$$d_1 = d(001) - d_2 = d(001) - 5.6 \quad (1)$$

$d(001)$  is easily determined from 001 reflections, which are well recognized in the X-ray powder pattern.

## 3.1. INTERCALATION PROCESSES

The intercalation of primary diamines,  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  was investigated for the members with  $n$  ranging from 0 to 12, with the exception of  $n = 11$ . Figure 2 shows the titration curves of ZrPP with some of these diamines. The curves have essentially a single inflection point around pH 7; the pH then rises to reach the buffered zone formed by the free diamines and their conjugated acids. The largest part of the curves, before the inflection point, lies below the initial pH of the diamine hydrochloride solution and hence some  $\text{H}^+ / (\text{CH}_2)_n(\text{NH}_3)_2^{2+}$  ion exchange has occurred concomitantly with the intercalation.

No determination of diamines taken up at different pH values has been performed but it is reasonable to suppose that, below the inflection point, practically all the added diamine molecules have been intercalated. This amount (2.0–

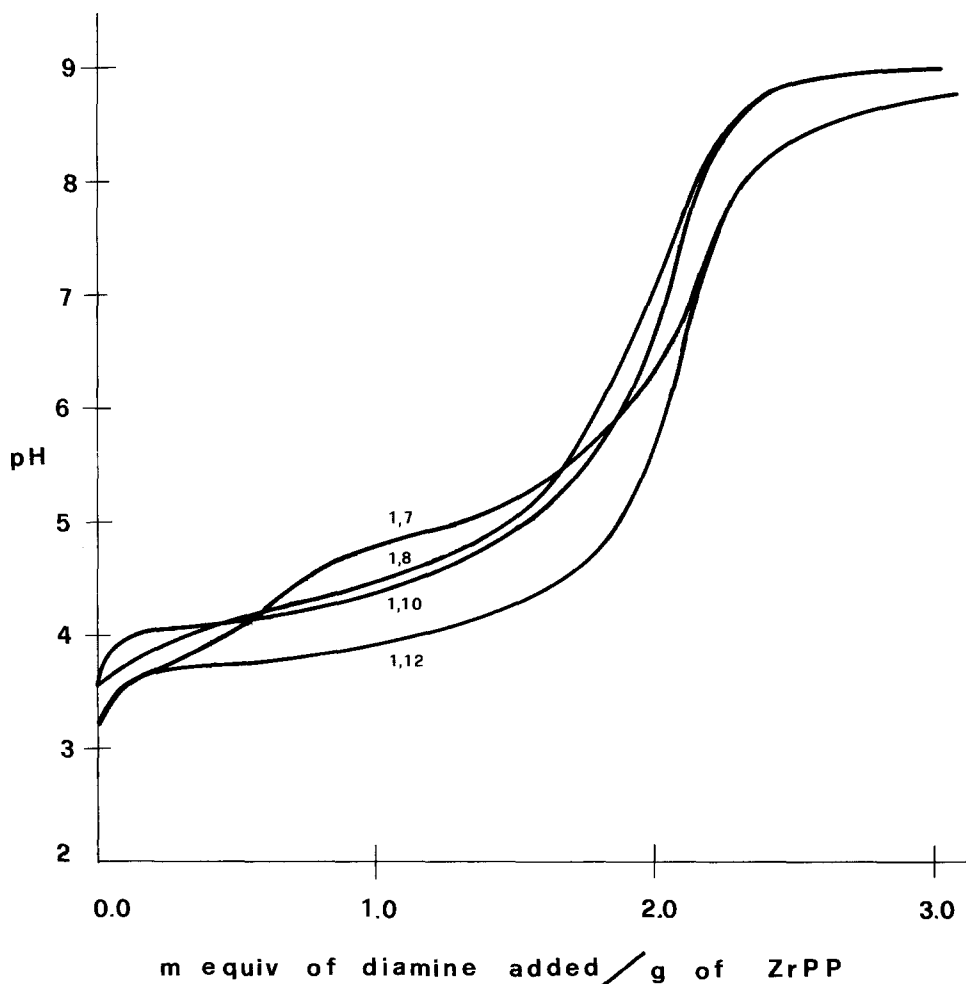


Fig. 2. Potentiometric titration curves of zirconium phosphate phosphite, in the presence of 0.050M alkyl diammonium hydrochloride, with 0.050M solution of the indicated diamines.

2.1 meq/g) is a little lower than the amount of phosphate groups in the solid (2.5 mmol/g), suggesting that the diamines are intercalated mostly as bibasic species, interacting with two phosphate groups belonging to two facing layers. However, due to the presence of ~30% of inert phosphite groups randomly distributed in the phosphate region, some of the diamine molecules could not have found two P–OH groups in the right position for the double protonation and therefore could be intercalated as monoprotinated species. If this is the case, free phosphate groups should be still present in the solid and it may be inferred that intercalation of diamines may still occur at high pH values, after the inflection point and even in the buffered zone. It has indeed been found that, when the host is equilibrated with a large excess of diamine solution, the amount intercalated, depending on the nature of the diamine, is in the range 2.8–3.7 meq/g corresponding to a value of  $y$ , see Table I, of 0.37–0.49. This clearly demonstrates that, when the diamines are forced to be intercalated, they are also present as monoprotinated species following the tendency to completely fill the interlayer volume created by the expansion of the layers.

The shape of the titration curves merits some comments. After an initial sharp increase in pH, the curves appear to be flat with a slight slope. No well-defined plateau is thus present, in contrast to the behaviour of lamellar hosts of the zirconium phosphate type. In the latter both ion exchange and intercalation usually occurs with a discontinuous change in the interlayer distance. Once an appreciable amount of the new phase is formed it grows as intercalation proceeds, at the expense of the starting one, with the movement of the phase boundary from the external part towards the core of the crystallites [9]. Until the two solid phases

Table I. Composition, interplanar spacing of 001 reflection,  $d(001)$ , and interlayer spacing of phosphate regions,  $d_1$ , for ZrPP fully intercalated with diamines

$\text{Zr}(\text{HPO}_4)_{0.7}(\text{HPO}_3)_{1.3}y(\text{NH}_2(\text{CH}_2)_n\text{NH}_2) \cdot m\text{H}_2\text{O}$				
$n$	$y^a$	$m^b$	$d(001), \text{Å}^c$	$d_1, \text{Å}^d$
0	0.43	0.6	14.77	9.17
2	0.36	1.3	15.81	10.21
3	0.37	2.0	16.58	10.98
4	0.37	1.6	18.48	12.88
5	0.38	2.2	19.24	13.64
6	0.39	2.2	20.81	15.21
7	0.49	3.2	21.59	15.99
8	0.42	1.9	22.99	17.39
9	0.46	2.1	23.67	18.07
10	0.42	1.0	25.30	19.70
12	0.45	1.3	27.72	22.12

<sup>a</sup> From elemental analysis.

<sup>b</sup> From TG–DTA coupled analysis.

<sup>c</sup> Average of the values measured on 2*d*–5th order of 001 reflections; e.s.d. = 0.03 Å.

<sup>d</sup> From Eq. (1).

coexist, no change in the composition of the equilibrating solutions occurs, provided the temperature and the pressure are kept constant. Accordingly, the titration curves show well-defined plateaux corresponding to the two phase regions.

The different behaviour of ZrPP and ZrP is evident from Figure 3, which compares the titration curves of the two host compounds with 1,6-diaminohexane, obtained under the same experimental conditions. In ZrP, intercalation starts at lower pH values and occurs via three different two-phase regions,

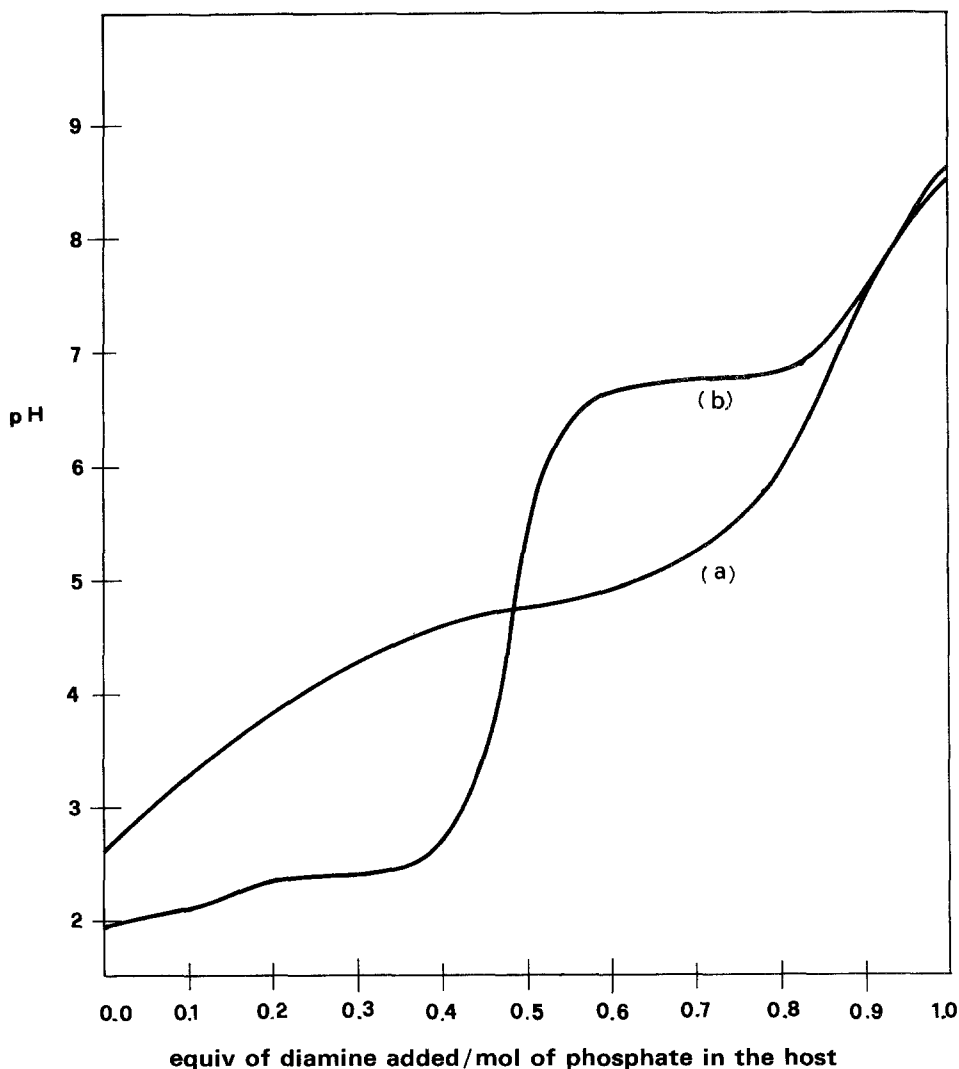


Fig. 3. Comparison between the titration curves of zirconium phosphate phosphite (curve a) and zirconium phosphate (curve b) with 1,6-diaminohexane (0.050M) in the presence of the corresponding hydrochloride (0.050M).

easily detectable in the titration curves. The first step corresponds to the formation of the  $\text{ZrP}\cdot 0.2 \text{C}_6\text{H}_{12}(\text{NH}_2)_2$  phase (interlayer distance,  $d = 10.7 \text{ \AA}$ ) having the diamine molecules probably oriented parallel to the layers. The half intercalated phase ( $\text{ZrP}\cdot 0.5 \text{C}_6\text{H}_6(\text{NH}_2)_2$  ( $d = 12.6 \text{ \AA}$ )) and the fully intercalated phase ( $\text{ZrP}\cdot \text{C}_6\text{H}_{12}(\text{NH}_2)_2$  ( $d = 15.4 \text{ \AA}$ )) are formed in the second and third step, respectively [10].

In contrast, intercalation in ZrPP seems to occur with a progressive saturation of the interlayer region, leading directly to the formation of the fully intercalated phase.

Actually, X-ray analysis of samples of ZrPP with increasing content of 1,6-diaminohexane shows a discontinuous transformation of the original ZrPP into a phase with  $d(001) = 16.3 \text{ \AA}$  ( $d_1 = 10.7 \text{ \AA}$ ), corresponding to  $\sim 30\%$  intercalation. The related XRD pattern is shown in Figure 4a. Though further addition of diamine does not cause a distinct rise of the pH of the solution, in the 30–50% range of intercalation the  $16.3 \text{ \AA}$  phase is readily transformed into a phase with  $d(001) = 20.6 \text{ \AA}$  ( $d = 15.0 \text{ \AA}$ ).

The latter value of  $d(001)$  is very close to the corresponding value measured in the pattern of the fully intercalated compound ( $20.81 \text{ \AA}$ ); see Figure 4b. Accordingly, the subsequent intercalation of diamine occurs without any further phase transition. Taking into account the X-ray data, the titration curve of ZrPP with 1,6-diaminohexane may be interpreted on the basis of the presence of narrow two-phase regions, not involving a sudden change in pH, and of a broad region in which intercalation occurs via a solid solution mechanism.

Intercalation of the other diamines in ZrPP should occur with the same mechanism, as suggested by the similarity of their titration curves and of X-ray data with those of 1,6-diaminohexane. The X-ray diffraction pattern of ZrPP fully intercalated with 1,12-diaminododecane is reported in Figure 4c.

The different mechanism of intercalation of diamines in ZrPP with respect to ZrP is probably related to the rigidity of the phosphite region-containing double layers, which separate two adjacent expandable phosphate regions. Accordingly, a little more energy is required to open the phosphate region of ZrPP (hence higher pH of initial intercalation), but once a perceptible amount of intercalated phase is formed, the process goes on preferably via a solid solution where ZrP prefers the phase transitions [5].

Intercalation of diamines in zirconium phosphate has been found to be a slow process [10] probably due to the fact that each elementary jump of the molecule within the interlayer region generally requires a concerted double protonation and deprotonation.

It may be seen from Figure 5 that the diffusion of diamines in the phosphate region of ZrPP is a very fast process compared to that observed in ZrP. The marked difference in diffusion rates is again related to structural differences between the two hosts that involve a different mechanism of intercalation. In both the compounds it is assumed that intercalation occurs with the movement of a phase-boundary, between the intercalated and original phases, towards the core of the microcrystals. The phase boundary in ZrPP should be much more extended than in ZrP, since the expandable phosphate regions in the former compound are separated by inert phosphite regions that render the layers thicker and more rigid. The presence of a

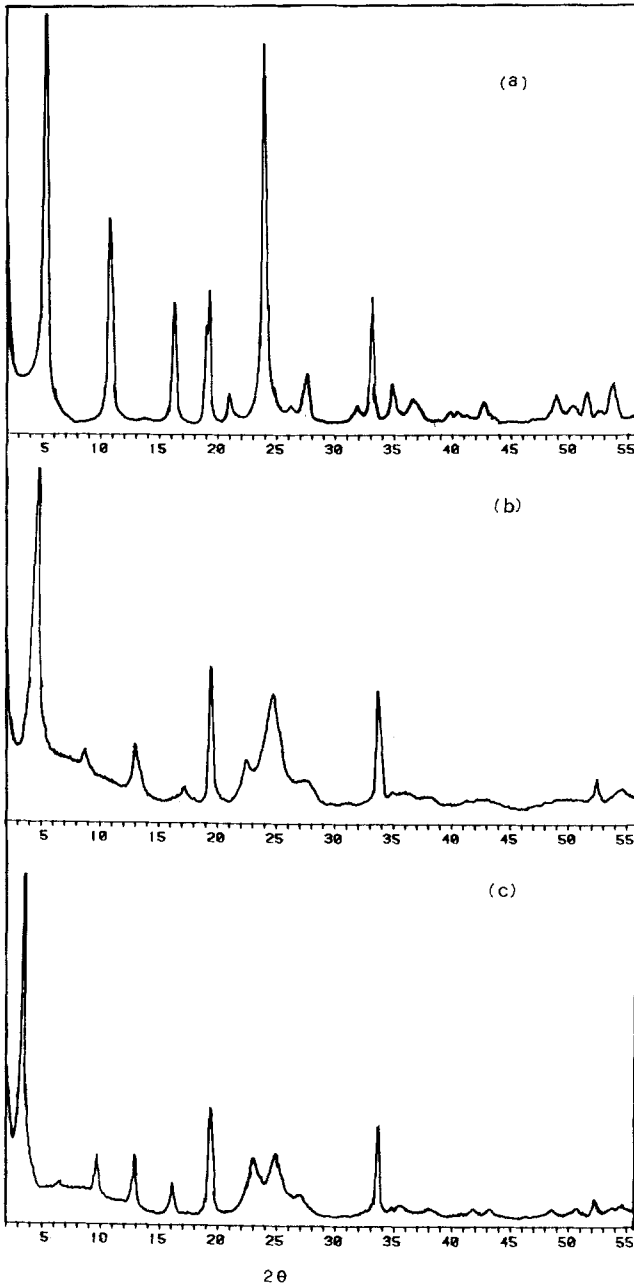


Fig. 4. X-ray patterns of intercalation compounds of zirconium phosphate phosphite:  
 (a)  $\text{Zr}(\text{HPO}_4)_{0.7}(\text{HPO}_3)_{1.3} \cdot 0.09 \text{NH}_2(\text{CH}_2)_6\text{NH}_2 \cdot 2.6 \text{H}_2\text{O}$ ;  
 (b)  $\text{Zr}(\text{HPO}_4)_{0.7}(\text{HPO}_3)_{1.3} \cdot 0.39 \text{NH}_2(\text{CH}_2)_6\text{NH}_2 \cdot 2.2 \text{H}_2\text{O}$ ;  
 (c)  $\text{Zr}(\text{HPO}_4)_{0.7}(\text{HPO}_3)_{1.3} \cdot 0.45 \text{NH}_2(\text{CH}_2)_{12}\text{NH}_2 \cdot 1.3 \text{H}_2\text{O}$ .



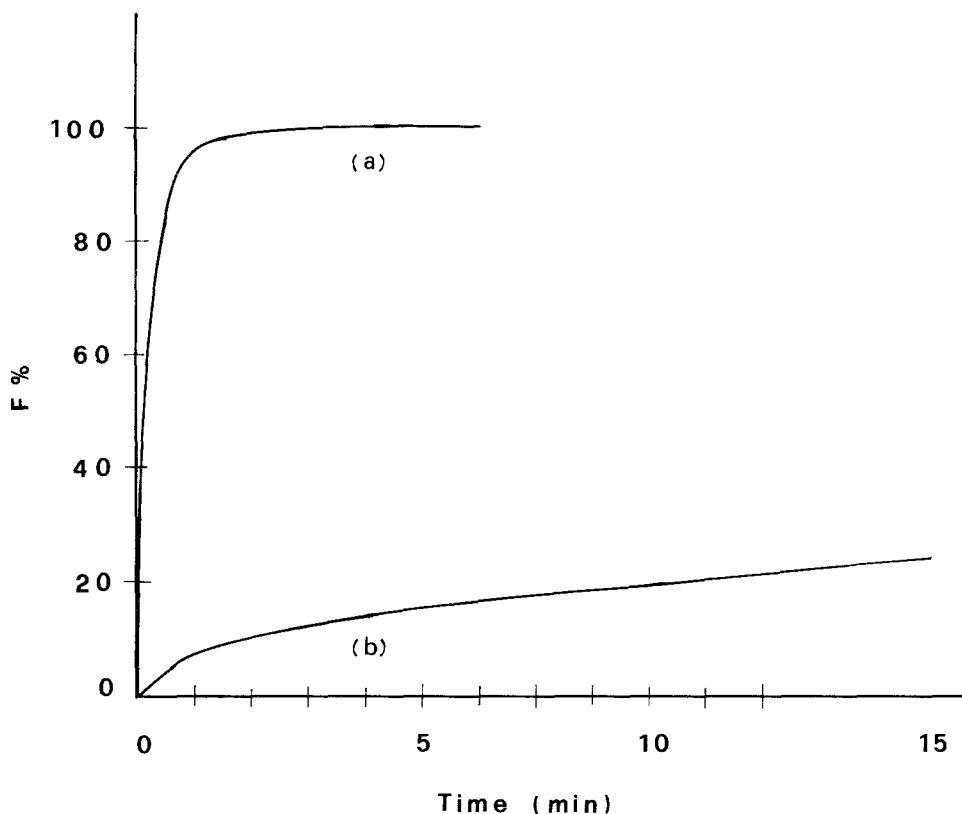


Fig. 5. Comparison between the intercalation rates of diamines in zirconium phosphate-phosphite (curve a) and in zirconium phosphate (curve b) at pH = 7 (20°C). The intercalation rates,  $F\%$  (mol of diamines intercalated at different times/mol of diamines intercalated at infinite time, per cent), have been determined using microcrystals of similar size.

diffuse phase boundary as well as of some phosphite groups in the phosphate regions, that act as defects, should be responsible for the high diffusion rate in ZrPP.

### 3.3. SOME CONSIDERATIONS ON THE ARRANGEMENT OF INTERCALATED DIAMINES

Table I reports the chemical composition of the fully intercalated alkyldiamine-ZrPP derivatives prepared by the batch procedure in an excess of diamine solution, together with the value of  $d(001)$  measured from the X-ray diffraction pattern.

Diamine molecules are arranged in monolayers within the phosphate regions, according to the variation displayed by the  $d_1$  spacing as a function of the number of methylene groups in the alkyl chain,  $n$  (see Table I and Figure 6). In particular, the odd-even effect (an increase of ca. 1.5 Å per CH<sub>2</sub> group, going from odd to even and of ca. 0.7 Å going from even to odd number of methylene groups) suggests the axis of the alkyl chain to be oriented in such a way that some of the C—C bonds, approximately one half, are located perpendicular to the layer plane. It is interesting

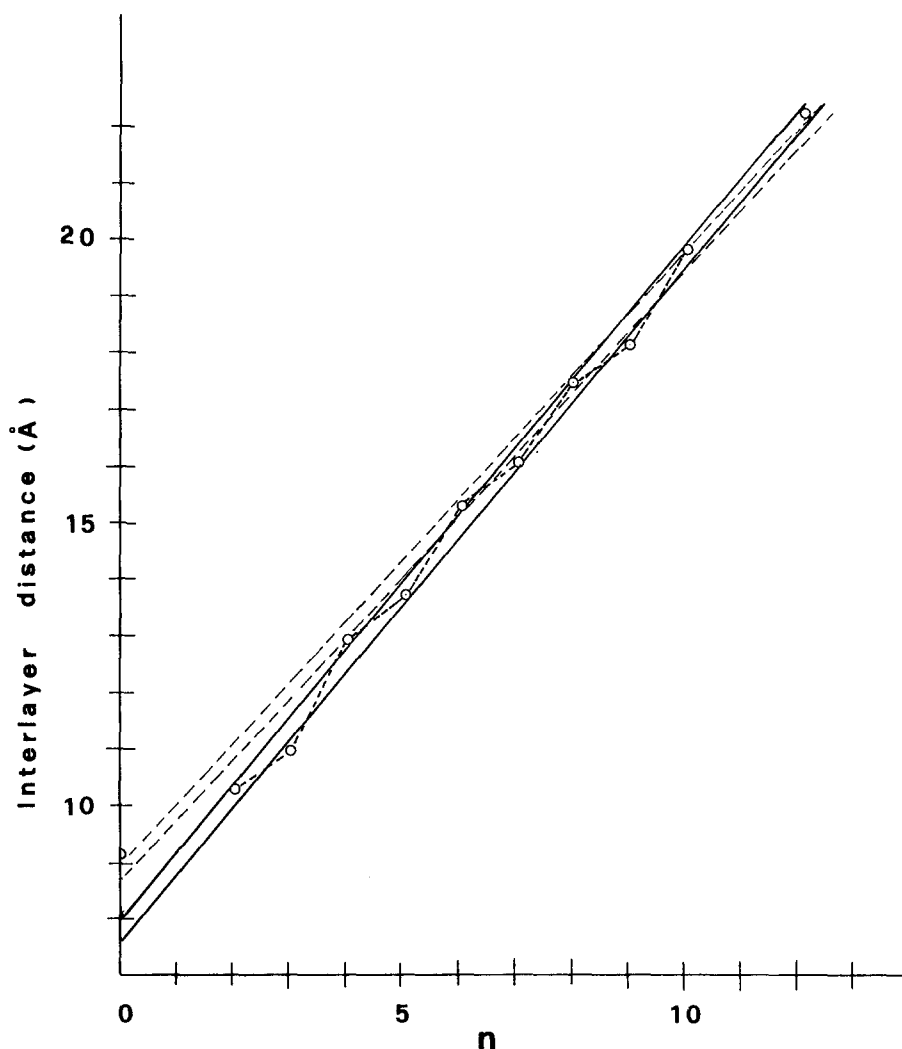


Fig. 6. Interlayer distance within the phosphate region of zirconium phosphate phosphite (full line) and interlayer distance of zirconium phosphate (dashed lines, data from Refs. [10] and [12]), fully intercalated with primary diamines,  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ , as a function of  $n$ .

to remark that an odd-even alternation has been recently reported for mono-alkylamine intercalation derivatives of ZrP [11].

Practically, when considering even and odd members separately,  $d_1$  is linearly related to  $n$  by the equations:

$$d_1 = d_0 + 1.18 n \quad (\text{n even})$$

$$d_1 = d'_0 + 1.18 n \quad (\text{n odd})$$

The values  $d_0$  and  $d'_0$  resulting from the regression of Figure 6 (correlation

coefficients higher than 0.99) are 8.03 and 8.76, respectively; the former represents the value  $n = 0$ , the latter represents the value for  $n = 1$ .

When considering the even numbers, the above mentioned orientation of diamine molecules fulfills the ideal geometry required by the  $sp^3$  hybridization of the protonated nitrogen (N—C bond perpendicular to the layer plane with three NH groups hydrogen bonded to three surrounding  $PO^-$  groups) for both terminal amino groups. For the odd members, this is possible for one of the two terminal groups only, the other having to be tilted *ca.*  $70^\circ$  off the ideal orientation. This fact by itself does not prevent the protonation of the second nitrogen, though geometrical restrictions arise for the  $NH\cdots O$  bonds being established, at least for two of the three N—H bonds. A possibility would exist of obtaining the suitable orientation for both N—C bonds, by assuming a nearly *gauche* conformation on two adjacent C—C bonds (internal rotation angles of  $+90^\circ$ ,  $+90^\circ$  or  $-90^\circ$ ,  $-90^\circ$ ). In this case, a significant reduction of the alkyl chain length, and consequently of the interlayer distance  $d_1$ , should be expected for the odd members with respect to the even members. The existence of conformations of this type in the intercalated diamine derivatives of ZrPP must be excluded on the basis of the trend observed for  $d_1$  values. Evidently, the increase of the cross section of the alkyl chain, due to the deviation from the extended conformation, is not tolerated by the crystal packing.

It is interesting to note the similarity of the trend of  $d_1$  for ZrPP and the corresponding trend for ZrP (see Fig. 6), according to the experimental data reported in [10] for even members of linear diamines. X-ray data recently obtained for some fully intercalated derivatives of ZrP with odd members of diamines [12] show the same odd–even effect found for ZrPP.

The similarity in the intercalation behavior of ZrPP and ZrP indicates for the former a tendency to reach the same packing density which is obtained for ZrP, in spite of the resulting lower concentration of acid sites within the phosphate-rich regions. In this way, the results listed in Table I, indicating that the moles of diamine intercalated in some of the samples prepared by the batch procedure exceed those expected on the basis of the dibasic behaviour, may be accounted for. In fact, in the presence of an excess of diamine, some molecules are certainly taken up as dibasic species, binding two phosphate groups located on the facing layers; these molecules should act as pillars while determining the interlayer separation. Other molecules may be intercalated as monobasic species or possibly as free bases to fill the interlayer volume.

In practice, for  $n \leq 6$ , the number of moles of diamine intercalated,  $y$ , is close to 0.35, the value corresponding to a dibasic behaviour of all the diamine molecules.

For  $n > 6$ , the experimental values of  $y$  are significantly higher than 0.35 with a tendency to reach the value of 0.5, corresponding to the total occupancy of the crystal sites available for intercalation. The latter feature is particularly evident for the odd members (see Table I). The remaining free volume, associated with residual unoccupied crystal sites ( $y$  remains generally below 0.5) is filled by water molecules. Accordingly, the water content for the diamine derivatives of ZrPP is significantly higher with respect to the corresponding derivatives of ZrP, [10] for which a total occupancy of the crystal sites occurs.

Finally, it is interesting to observe that the  $d_1$  value of the hydrazine intercalation compound (9.17 Å) is a little higher than the intercept value (8.03 Å) of the line of

even members. Very likely only one amine group of this guest is protonated and the other interacts with weaker hydrogen bonds giving rise to a longer bond.

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