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Intercalation of Heterocyclic Compounds in α-Zirconium Phosphate: Imidazole, Benzimidazole, Histamine and Histidine

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Abstract. The intercalation of imidazole and some organic species containing the imidazole ring, between the layers of crystalline zirconium phosphate has been investigated. Fourteen new, well-ordered intercalation compounds are obtained with the batch procedure at r.t. and/or 60°C. A mechanism of formation of the various compounds is proposed on the basis of the interaction between the guest molecules (with their dimensions and geometries) and the free PO_3OH groups available between the layers of the host. The new phases have been characterized by TG and X-ray methods.

Key words: Zirconium phosphate, imidazole, benzimidazole, histamine, histidine, intercalation.

1. Introduction

Studies on the intercalation behaviour of layered α-zirconium phosphate, α-$[Zr(PO_4)_2]H_2 \cdot H_2O$, have shown that various kinds of polar organic molecules can be accommodated in the interlayer space. Some guests such as alcohols and glycols, are held to the inorganic host through weak bonds (van der Waals interactions or hydrogen bonds), others such as monoamines and diamines, are bonded with ionic interactions. In the fully-intercalated phases, monofunctional guests are usually arranged as a bimolecular layer while the bifunctional ones form a monolayer.

Stoichiometric intercalation compounds of formula α-$[Zr(PO_4)_2]H_2 \cdot 2I$ (I being a monofunctional intercalated species) are obtained only if the cross-section of the guest molecules is less than the free area (24 $Å^2$) surrounding each phosphate group. Notwithstanding this general picture recently outlined in monographs and reviews [1–3], studies on the intercalation chemistry of α-$[Zr(PO_4)_2]H_2 \cdot H_2O$ and other insoluble acid salts of tetravalent metals are still in their infancy.

For example, apart from a paper dealing with the intercalation of aminoacids [4], little is known regarding interactions of complex species bearing two or more functional groups, or of species of biopharmaceutical interest with α-zirconium phosphate. Nonetheless, the

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intercalation of these species is of interest in order to further clarify the intercalation chemistry of α-zirconium phosphate and because they lead to the preparation and characterization of new intercalated phases. These phases form a rich material suitable for studying the interlayer organization of intercalated species and of host-guest interactions, as well as for potential use in the field of storage of active species, of phase-transfer catalysis and drug-release. Finally, taking into account the structural analogies between α-zirconium phosphate and smectite clays [5, 6] and the extensive literature on, and increasing interest in, the clay-organic systems [7, 8], the information derived from the intercalation chemistry of α-zirconium phosphate could help in the interpretation of the intercalation chemistry in clays.

The present paper reports on the study of the intercalation mechanism in α-zirconium phosphate of some organic species containing an imidazole ring in their structure, and the characterization of the intercalation compounds obtained.

2. Experimental

2.1. MATERIALS

C.Erba RPE reagents were used, except for $ZrOCl_2 \cdot 8H_2O$ which was a Merck 'pro analysi' product and the organic compounds which were supplied by Fluka.

Microcrystals of α-$[Zr(PO_4)_2]H_2 \cdot H_2O$ (referred to as $ZrPH_2$) were obtained by passing a pre-humidified air stream into a solution containing zirconium fluorocomplexes and phosphoric acid according to the HF procedure [9]. The hydrogen-sodium form α-$[Zr(PO_4)_2]HNa \cdot 5H_2O$ (ZrPHNa) and the ethanol complex α-$[Zr(PO_4)_2]H_2 \cdot 2EtOH$ (ZrPEt) were prepared as described in [10] and [11]. These materials are also referred to by their interlayer spacing, which is 7.6, 11.8 and 14.2 Å, respectively. The same notation is adopted for the intercalation compounds.

2.2. INTERCALATION PROCEDURE

The intercalation procedure used was the batch technique at room temperature and/or 60° C. The operating conditions such as solid/solution ratios, concentration of the solutions, temperature, etc., will be given in detail in the results section, since they depend on the host material and the guest organic compound. Aqueous solutions of the organic compounds were used at concentrations ranging between 0.1 and 0.01 mol dm^{-3}. Due to the low solubility of benzimidazole at r.t., the 0.1 mol dm^{-3} solutions of this compound were prepared and stored at 60° C. When ZrPHNa was employed, the pH of the organic solutions was, in some cases, lowered to the desired value by adding HCl. The equilibrium time was determined by monitoring the concentration change of the organic species in the supernatant liquid. When no further uptake was apparent, the solids were filtered off and the solutions analyzed for pH, organic compound, phosphate and (when ZrPHNa was used) sodium content. X-ray diffractograms of wet and air-dried solids were taken to follow the phase changes undergone after uptake. The intercalation compounds were also characterized by TG and TDA measurements, in order to determine their water content and the temperature of decomposition of the organic guests. At the same time, since ignition up to 1200° C of the intercalates not containing sodium ion always lead to cubic ZrP_2O_7, it was possible to check the composition in organic guest from the weight loss at this temperature.

2.3. ANALYTICAL PROCEDURE AND APPARATUS

The concentrations of the amine solutions before and after contact were determined potentiometrically with standard HCl solutions on a Metrohm Herisau Potentiograph model E 436. Imidazole and benzimidazole were also determined spectrophotometrically at 216 and 245 nm, respectively, on a Perkin-Elmer 550 S Spectrophotometer. The concentration of the histidine solutions was determined by the ninhydrin colorimetric method, suitably modified. In order for the Lambert–Beer law to be valid, the histidine solutions were first diluted to a concentration of *ca.* $1\text{–}10 \times 10^{-4}$ mol dm^{-3}. The reactant was prepared by mixing equal volumes of solution A (2% of ninhydrin in ethylene glycol) and solution B (0.2% of $SnCl_2$ in sodium citrate buffer at pH 5). The mixture was left to stand for 20 min before use. Exactly 5 ml of the reactant were added to 1 ml of the histidine solution and the mixture heated in boiling water for 20 min. After cooling, the solution was diluted to 25 ml and, within 20 min, the absorbance read at 570 nm against a blank.

The phosphates possibly released from the host to the solution by hydrolytic attack, were determined spectrophotometrically at 430 nm by the phosphomolybdic method. Sodium ions were determined by flame photometry with a Techtron-Varian A.A.120 spectrophotometer. The pH measurements were made with a Beckman Research pH meter model 1019.TG-DTA analyses of the intercalation compounds were performed with a Mettler 2000 °C thermoanalyzer at heating rate of 5 °C min^{-1} in an air flow. The X-ray diffraction patterns were taken on a Philips diffractometer using Ni-filtered Cu$K\alpha$ radiation.

3. Results

Before describing the results, it is helpful to recall some features of the chemistry of the host system. The crystal structure of α-zirconium phosphate, as determined by Clearfield and Smith [12], is a layered one. Each layer consists of zirconium atoms lying nearly in a plane ($\pm$ 0.25 Å) and bridged through phosphate groups alternatively situated above and below the zirconium atom plane. Three oxygen atoms of each phosphate group are bonded to three different zirconium atoms and the fourth oxygen, bears a proton. Each layer may be considered as a planar macromolecule of $[Zr_n(PO_4)_{2n}]H_{2n}$. The planar density of the tetrahedral PO_3OH groups on each side of the layer is one group per 24 Å^2 and the thickness of the layer calculated at the top of the P—OH groups anchored on the opposite sides of the layer is ~9 Å. The interlayer distance in the crystals of α-$[Zr(PO_4)_2]H_2 \cdot H_2O$ is 7.6 Å so there is a certain copenetration between the P—OH groups belonging to two adjacent layers. This tight packing creates a strong steric hindrance to the diffusion in the interlayer region of species with a cross-sectional diameter larger than 2.6 Å [12]. Organic molecules cannot, generally, diffuse, or they diffuse very slowly. However, when these molecules are bases, they have a strong tendency to protonate inside the crystals of α-$[Zr(PO_4)_2]H_2 \cdot H_2O$ causing the layers to spread apart and the organic bases to diffuse in the interlayer region.

In contrast to what occurs in graphite and in some layered dichalcogenides, the intercalation does not take place by stages but it seems to proceed concomitantly in each interlayer region. The diffusion begins at the edges and proceeds towards the bulk of the crystallites with an advancing phase boundary, so that during the intercalation process, both the original hydrogen form and the new intercalate phase co-exits in the same crystal, as shown schematically in Figure 1a. The full intercalation of an organic base generally results in a progressive saturation of the active sites – the PO_3OH groups – with discontinuous changes in the interlayer distance, since phases of different composition (saturation of one quarter,

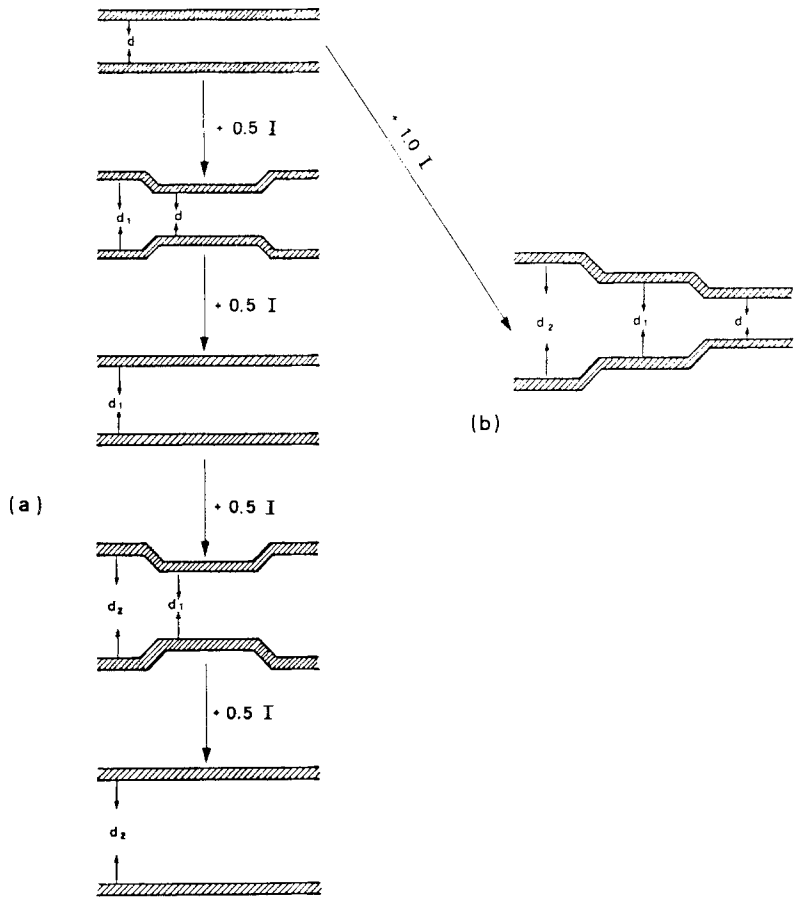


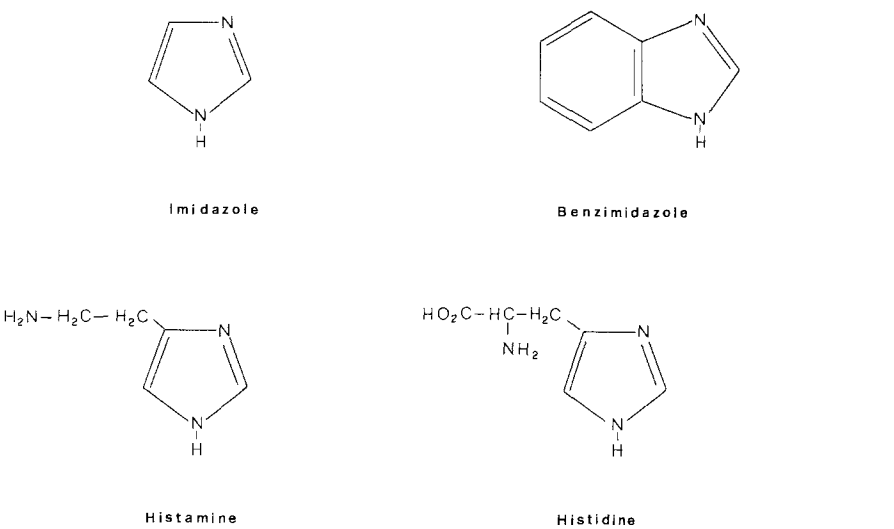
Fig. 1. Schematic representation of the intercalation mechanism of a monofunctional guest (I) in α-$[Zr(PO_4)_2]H_2 \cdot H_2O$: (a) slow addition of the guest: intercalation occurs stepwise and only two phases are eventually present in the same crystallite; (b) rapid addition of the guest: more than two phases can simultaneously be present in the same crystallite.

half, three quarters of the active sites) are formed before the fully-intercalated phase is obtained [3]. It often occurs that before a given phase has been transformed into another, a new intercalate phase begins to form at the edge of the crystallites (see Figure 1b), so that the X-ray diffraction patterns show the simultaneous presence of three (or more) different phases. From this situation of disequilibrium, the system goes to equilibrium with a very slow solid-state reaction, especially if there is a large activation energy barrier for the translational motion of the guest. To avoid these supersaturation phenomena and to have a pure intercalation compound via a two-phase transition, it is necessary to furnish the guest molecules to the host system very slowly and, in some cases, at a relatively high temperature. If necessary, the intercalation compound may be prepared by using as hosts some derivatives of α-zirconium phosphate having a large interlayer distance such as the polyhydrated zirconium phosphate, α-$[Zr(PO_4)_2]H_2 \cdot 5H_2O$ (d = 10.4 Å) and the half exchanged sodium form, α-$[Zr(PO_4)_2]HNa \cdot 5H_2O$ (d = 11.8 Å) or some alcohol intercalated phases (e.g., α-$[Zr(PO_4)_2]H_2 \cdot 2EtOH$ (d = 14.2 Å). The large interlayer distance and the consequent

decrease of the attraction between adjacent layers, together with the presence in the interlayer region of weakly bonded species (water, alcohols), greatly favours the diffusion of the organic bases in the interlayer region, and the intercalation generally proceeds without the mentioned supersaturation phenomena.

Bearing in mind these general considerations on the intercalation chemistry of α-zirconium phosphate, the intercalation procedure for the organic compounds examined here has been sometimes performed at 60 °C and/or the mentioned derivatives of $ZrPH_2$ with large interlayer distances have been employed.

We now illustrate the results obtained for each of the guest molecules whose structural formulae, for the reader's convenience, are reported in Scheme **1**.



Scheme **1**. Structural formulae of the four guest bases.

3.1. IMIDAZOLE

The intercalation of imidazole (Im) is simply achieved by titrating $ZrPH_2$ suspended in water with a 0.1 mol dm^{-3} aqueous solution of the heterocyclic base at r.t. The titration curve (see Figure 2) shows only one plateau at a constant pH of 6.5, with the end point occurring when 3.2 mmol of Im/g of $ZrPH_2$ (*ca.* 1 mol of Im/mol of exchanger) are added. X-ray analysis of solid samples containing increasing amounts of Im shows that the intercalation occurs with a single phase transition, since the starting $ZrPH_2$ is transformed into a phase with an interlayer distance of 10.9 Å until a loading of 0.75 mol of Im per mole of host is reached. Further intercalation of Im occurs *via* a solid solution mechanism and leads to an intercalation compound of composition α-$[Zr(PO_4)_2]H_2$ 0.8Im $1.3H_2O$. This final compound is also obtained when 100 ml of 0.1 mol dm^{-3} Im solution are equilibrated with an amount of ZrPEt equivalent to 1 g of $ZrPH_2$.

Attempts to obtain a more loaded Im phase by increasing the temperature and/or the volume-mass ratio were unsuccessful. Table I reports the *d*-values obtained from the X-ray diffraction pattern of α-$[Zr(PO_4)_2]H_2$ 0.8Im $1.3H_2O$.

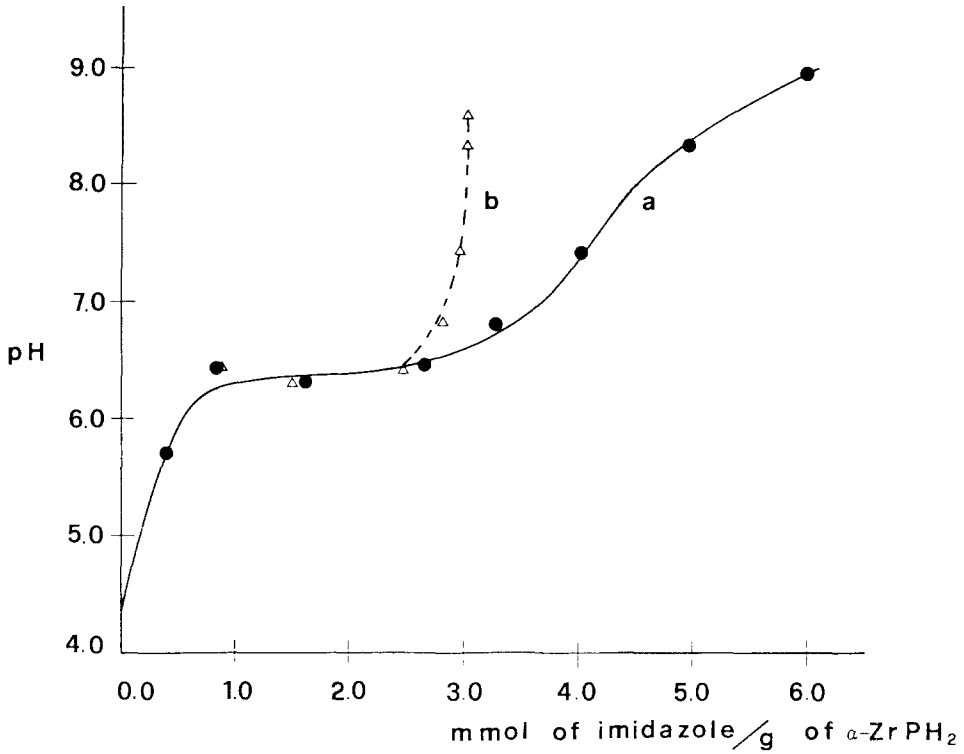


Fig. 2. Titration (a) and uptake (b) curves obtained by titrating α-$[Zr(PO_4)_2]H_2 \cdot H_2O$ with a 0.1 mol dm^{-3} solution of imidazole at 25 °C.

3.2. BENZIMIDAZOLE

Benzimidazole (Bim) was intercalated by adding increasing volumes of 0.1 mol dm^{-3} aqueous solution of Bim to several samples of $ZrPH_2$ (1 g) at 60 °C. The mmol of Bim intercalated are plotted against those added in Figure 3.

The X-ray powder patterns of the solid samples reveal that full intercalation occurs *via* four successive phase transitions and the intercalation process may be represented by the following scheme, in which the solubility of guest molecules in the previously formed phases has been neglected:

$$ZrPH_2\ (7.6\ \text{Å}) \longrightarrow ZrPH_20.4\text{Bim}\ nH_2O\ (11.3\ \text{Å}) \longrightarrow ZrPH_20.57\text{Bim}\ 2.25H_2O\ (13.6\ \text{Å}) \longrightarrow ZrPH_21.4\text{Bim}\ 2.1H_2O\ (18.7\ \text{Å}) \longrightarrow ZrPH_21.9\text{Bim}\ 1.5H_2O\ (20.4\ \text{Å}).$$

All the mentioned phases have been isolated as pure intercalation compounds, except the 11.3 Å phase which is always present together with the 7.6 or 13.6 Å phases. Its composition has been estimated *via* a knowledge of the amount of guest intercalated, of the composition of the pure 13.6 Å phase and assuming that the intensities of the X-ray reflections corresponding to the interlayer distances were proportional to the amounts of the relative phases present.

Intercalation of Bim is also easily performed by equilibrating the ZrPEt phase with aqueous solutions of the heterocyclic base.

Table I. X-ray diffraction patterns of imidazole and benzimidazole-zirconium phosphate intercalation compounds

$ZrPH_20.8Im \cdot 1.33 \cdot H_2O$		$ZrPH_20.75Bim \cdot 2.25H_2O$		$ZrPH_21.4Bim \cdot 2.1H_2O$		$ZrPH_21.9Bim \cdot 1.5H_2O$	
d (Å)	I	*d* (Å)	I	*d* (Å)	I	*d* (Å)	I
10.9	vs	13.6	vs	18.7	vs	20.4	vs
5.45	m	6.80	s	9.32	m	10.15	s
4.55	vw	4.63	mw	6.19	mw	6.75	m
4.47	m	4.52	w	4.65	w	5.04	w
4.13	w	4.29	w	4.59	m	4.43	m
3.80	m	4.05	mw	4.34	w	4.09	m
3.75	s	3.72	m	4.25	m	3.69	m
3.08	mw	3.45	mw	3.93	w	3.29	m
3.03	m	3.38	w	3.81	m	3.16	vw
2.69	w	3.14	w	3.58	mw	2.94	vw
2.68	mw	2.90	vw	3.53	w	2.68	mw
2.60	vw	2.69	w	3.47	mw	2.65	w
		2.65	m	3.36	m	2.59	vw
		2.42	vw	3.16	vw		
				3.09	vw		
				3.05	w		
				3.03	vw		
				2.96	w		
				2.69	w		
				2.67	m		
				2.63	w		
				2.59	vw		

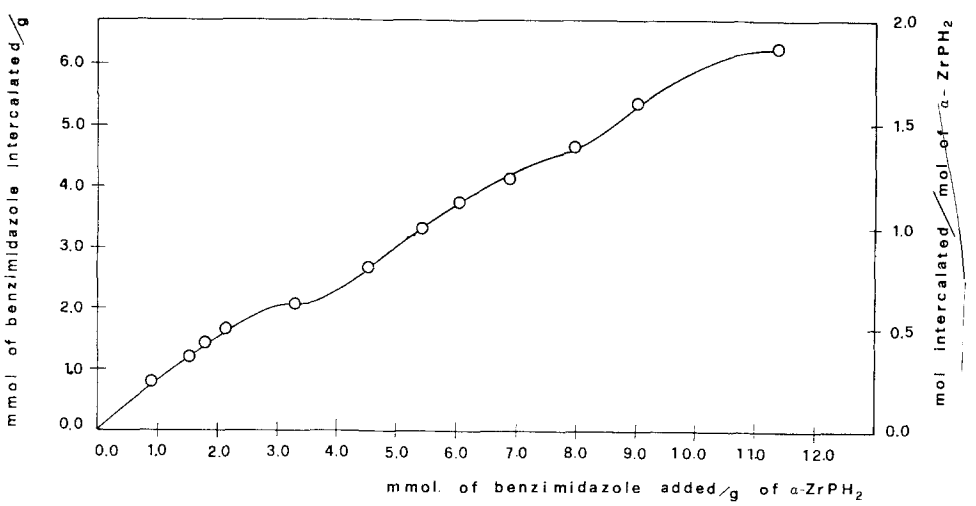


Fig. 3. Intercalation (uptake curve) of benzimidazole in α-$[Zr(PO_4)_2]H_2 \cdot H_2O$, at 60 °C.

X-ray diffraction patterns of all the intercalates obtained, except the 11.3 Å phase, are reported in Table I.

3.3. HISTAMINE

For the intercalation of histamine (Him), increasing volumes of 0.01 mol dm^{-3} Him solution were contacted with several samples of $ZrPH_2$ (1 g). The uptake curves at 25 °C (curve b) and 60 °C (curve a) are given in Figure 4. A limited amount of Him is intercalated at r.t. and only the pure phases of composition $ZrPH_2$ 0.33Him 1.65 H_2O (10.6 Å) and $ZrPH_2$ 0.67Him 2H_2O (12.4 Å) are obtained. At 60 °C and for equilibration times ranging between 2 and 20 days, the process goes almost to completion and a final phase containing 1.9 moles of Him per mole of host is formed. Taking into account the analytical and X-ray data, the intercalation process at 60 °C can be synthesized in five steps as in the scheme:

$ZrPH_2$ (7.6 Å) ⟶ $ZrPH_2$0.33Him 1.65H_2O (10.6 Å) ⟶
⟶ $ZrPH_2$0.67Him 2.1H_2O (12.9 Å) ⟶
⟶ $ZrPH_2$ 1Him 2.1H_2O (14.7 Å) ⟶
⟶ $ZrPH_2$1.25Him $n$$H_2O$ (16.3 Å) ⟶
⟶ $ZrPH_2$1.9Him 2.2H_2O (20.5 Å)

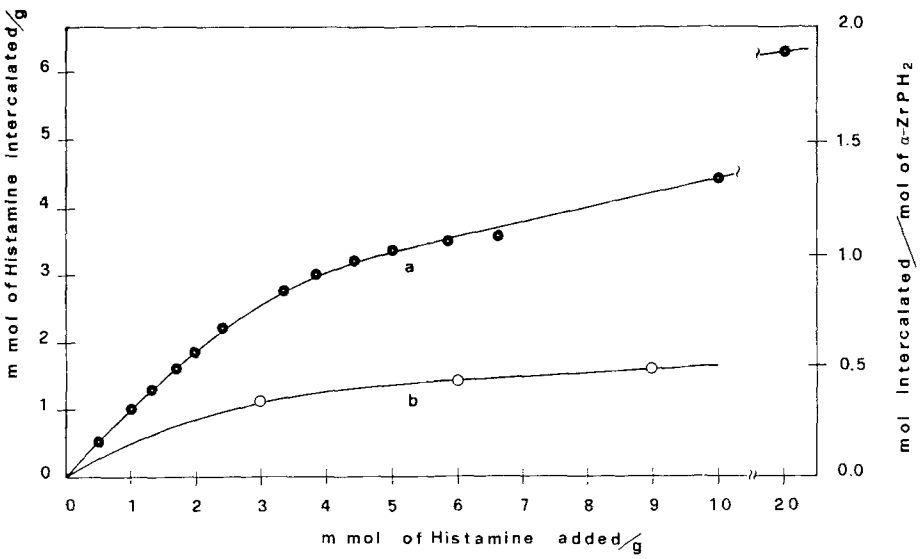


Fig. 4. Intercalation (uptake curve) of histamine in α-$[Zr(PO_4)_2]H_2 \cdot H_2O$, at (a) 60 °C and (b) 25 °C.

The fourth phase transition never leads to the pure 16.3 Å phase, since the 20.5 Å phase begins to form before the 14.7 Å phase is completely transformed into the 16.3 Å one. The composition of the 16.3 Å phase has been roughly estimated from analytical and X-ray data as described for the 11.3 Å-Bim phase. The 20.5 Å phase is more easily obtained at r.t. by contacting 1 g of ZrPEt with 100 ml of 0.1 mol dm^{-3} Him solution.

Employing ZrPHNa (11.8 Å) as the starting material and contacting with 0.1 mol dm^{-3} Him solution at pH 3.5 even in large volumes, the 10.6 Å phase alone is formed and all the sodium ions initially present in the host lattice are released to the solution. Histamine intercalation does not occur when ZrPHNa is contacted with a solution of free base.

All the ZrP-Him intercalates give X-ray patterns as expected for well-ordered materials. Table II reports the *d*-values of the compounds obtained as pure phases.

Table II. X-ray diffraction patterns of histamine-zirconium phosphate intercalation compounds

$ZrPH_20.33Him \cdot 1.65H_2O$		$ZrPH_20.67Him \cdot 2.1H_2O$		$ZrPH_21Him \cdot 2.1H_2O$		$ZrPH_21.9Him \cdot 2.2H_2O$	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
10.6	vs	12.9	vs	14.7	vs	20.5	vs
5.29	m	6.47	m	7.36	m	10.25	s
4.48	w	4.54	vw	4.80	w	6.85	m
4.35	w	4.39	vw	4.64	vw	4.57	w
4.00	vw	4.05	w	4.41	mw	4.39	vw
3.77	m	3.96	w	4.34	vw	4.09	mw
3.63	mw	3.86	w	3.96	mw	3.61	w
3.21	vw	3.81	w	3.90	m	3.31	w
3.03	w	3.75	vw	3.42	vw	2.95	vw
2.93	w	3.69	vw	3.38	w	2.64	w
2.69	vw	3.43	w	3.35	mw	2.62	w
2.57	w	3.33	w	2.89	vw	2.56	vw
2.60	vw	3.26	vw	2.83	vw		
		3.20	vw	2.68	w		
		2.68	vw	2.63	vw		
		2.60	vw				

3.4. HISTIDINE

By contacting $ZrPH_2$ (0.5 g) with a 0.01 mol dm^{-3} solution (0.5l) of histidine (His), the intercalation compound $ZrPH_20.5His\ 2H_2O$ alone is obtained. The material is well ordered, with an interlayer spacing of 12.3 Å (Table IV). Attempts to obtain intercalates with larger His contents by increasing the volume/mass ratio and/or the concentration of the His solution, were unsuccessful. With 0.1 mol dm^{-3} His solution, the host swells considerably and the wet or dried material seems amorphous to the XRD. A similar phenomenon is observed when ZrPEt is equilibrated with 0.01 mol dm^{-3} His solutions at 25 °C. In this case, however, the air-dried solid with composition close to $ZrPH_20.9His\ 2H_2O$ shows a broad X-ray reflection at 16.2 Å.

Kijima *et al.* [4], who investigated the intercalation of His in a $ZrPH_2$ preparation having a degree of crystallinity lower than that employed in this work, were not able to obtain $ZrPH_20.5His\ 2H_2O$ as a pure phase and in the range 0.67–1.18 mole of His per mole of host, they obtained amorphous materials.

Table III. Intercalation compounds obtained by equilibrating α-ZrPHNa with histidine solution at 60 °C and various experimental conditions

His conc. (mol dm^{-3})	Initial pH	Volume / mass (dm^3/g)	Equilibrium time	Composition and interlayer distance of the intercalation compounds
0.01	7.65	1	7 d	$ZrPH_{1.85}Na_{0.15}0.17His \cdot 2H_2O$(9.4 Å)
0.01 (25 °C)	7.65	1	2 d	$ZrPH_{1.24}Na_{0.76}0.17His \cdot 3.8H_2O$(10.4 Å)
0.1	3–4	0.4	2 d	$ZrPH_20.5His \cdot 2H_2O$(12.3 Å)
0.1	5	0.4	6 d	$ZrPH_{1.9}Na_{0.1}0.66His \cdot 2H_2O$(13.2 Å)
0.1	7.75	0.4	2 d	$ZrPH_{1.1}Na_{0.9}0.95His \cdot 2H_2O$(15.1 Å)

Table IV. X-ray diffraction patterns of histidine intercalation compounds obtained from $ZrPH_2$ and ZrPHNa

$ZrPH_20.5His \cdot 2H_2O$		$ZrPH_20.9His \cdot 2H_2O$		$ZrPH_{1.85}Na_{0.15}0.17His \cdot 2H_2O$		$ZrPH_{1.24}Na_{0.76}0.17His \cdot 3.8H_2O$		$ZrPH_{1.9}Na_{0.1}0.66His \cdot 2H_2O$		$ZrPH_{1.1}Na_{0.9}0.95His \cdot 2H_2O$	
d (Å)	I	*d* (Å)	I	*d* (Å)	I	*d* (Å)	I	*d* (Å)	I	*d* (Å)	I
12.3	vs	16.2	s	9.4	vs	10.4	vs	13.3	vs	15.1	vs
6.10	m	8.26	m	4.71	m	5.21	ms	6.55	s	7.55	ms
4.61	w	5.52	w	4.59	w	4.34	vw	4.60	mw	5.06	mw
4.50	m	5.18	w	4.41	vw	4.00	w	4.51	m	4.70	mw
4.42	m	4.48	m	3.96	m	3.91	vw	4.05	mw	4.59	w
4.16	w	4.37	mw	3.79	w	3.27	mw	4.01	m	4.46	mw
3.98	ms	4.27	mw	3.64	mw	3.21	mw	3.95	m	4.37	w
3.92	ms	3.86	m	3.54	w	3.15	mw	3.90	m	4.20	mw
3.80	ms	3.78	ms	3.11	ms	2.71	vw	3.41	m	4.13	w
3.70	mw	3.71	ms	3.03	vw	2.64	w	3.28	mw	4.01	vw
3.57	vw	3.61	mw	2.92	vw	2.59	vw	2.65	m	3.67	m
3.49	mw	3.40	mw	2.77	w			2.63	mw	3.49	m
3.38	w	3.30	mw	2.74	w			2.61	w	3.32	vw
3.32	m	3.24	w	2.70	w					3.19	w
3.21	m	3.16	w	2.64	vw					3.09	mw
3.16	mw	3.03	vw	2.60	vw					3.02	vw
3.07	w	2.87	vw							2.99	mw
2.93	vw	2.64	ms							2.92	vw
2.83	vw	2.53	w							2.88	vw
2.75	w									2.74	vw
2.71	vw									2.69	w
2.66	m									2.65	w
2.63	m									2.58	w
2.65	w										

With ZrPHNa, His gives various well-ordered intercalation compounds, some containing sodium ions. The preparation of the different pure phases requires a careful control of various parameters, such as His concentration, temperature, equilibrium time, etc. For simplicity, Table III reports the experimental conditions for obtaining the listed phases. The X-ray diffraction patterns of the intercalates obtained from $ZrPH_2$ and ZrPHNa are given in Table IV.

3.5. THERMAL BEHAVIOUR OF THE INTERCALATION COMPOUNDS

All the intercalation compounds have been characterized from their thermal behaviour. The thermal decomposition generally takes place in three stages: dehydration, deintercalation of the organic base and condensation of the P—OH groups of the host. Nevertheless, the mode of thermal deintercalation of the guest is strongly affected by the nature of the base and the degree of intercalation, and a complete elucidation of the thermal behaviour of these new intercalation compounds requires further experimental work (XRD at different temperatures, IR analysis) that will be reported elsewhere.

As an example, Figure 5 shows the TGA and DTA curves of the intercalation compounds with the examined bases at the lower content. The dehydration step is clearly evident in all the samples, while the weight loss due to the decomposition of the base is superimposed on that due to condensation of the P—OH groups. The temperature of initial deintercalation ranges between 200 and 320°C (200°C for Bim, 220°C for His, 250°C for Im and 320°C for Him) and the reaction is accompanied by an endothermic effect immediately followed by an exothermic one probably attributable to the gradual elimination of carbonaceous moieties in the air flow. These exothermic reactions superimpose the endothermic effect expected in the range 400–600°C for the condensation of the phosphate groups. The final product is ZrP_2O_7 which crystallizes as a cubic phase at *ca.* 950–1000°C. The complete elimination of traces of carbon is obtained at temperatures higher than 1100°C.

4. Discussion

The present investigation has confirmed that α-zirconium phosphate is an excellent intercalating agent for very weak or bulky Brönsted bases.

The intercalation reactions, carried out under mild conditions, do not cause appreciable disorder of the host which remains unaltered with respect to its structure and composition (the loss of phosphate groups due to hydrolytic attack was neglegible in all the cases). These reactions may thus be considered simple topotactic solid-state reactions which occur stepwise. The X-ray powder patterns of the intercalates containing increasing amounts of a given guest molecule do not show 001 reflections attributable to phases arising from the 'staging' sequence found in the intercalation reactions in graphite and in some dichalcogenides [13]. The steps of intercalation are, indeed, to be connected to the formation of phases each being a stage 1 compound and having the interlayer region progressively saturated by the guest species, as sketched in Figure 1.

The 14 new intercalation compounds obtained in the present study have a degree of crystallinity generally comparable with that of the host, as deduced from the X-ray patterns which show sharp and well-defined *hkl* reflections. The 001 reflections enhanced in intensity because of strong preferential orientation effects, are present up to the fourth harmonic and are indicative of a good stacking order in the *c* direction. Only the compound

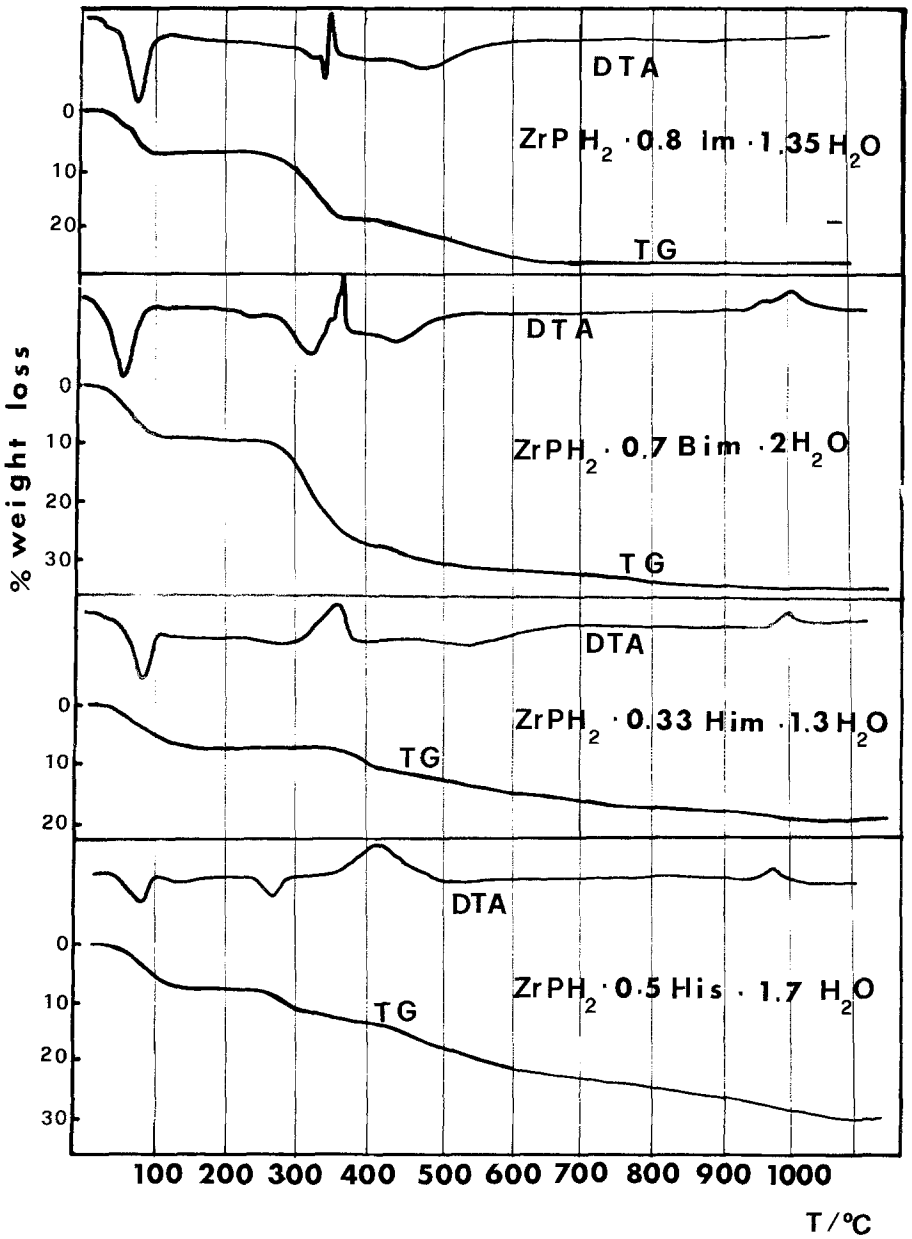


Fig. 5. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) curves of the indicated intercalation compounds.

$ZrPH_20.9His\ 2H_2O$ shows a low crystallinity and a reduction in particle size since the 001 reflections are few and very broad.

From the TGA data it can be seen that the temperature of initial deintercalation of the guests is generally higher than the m.p. of the pure bases Him (85°C); Im (90°C); Bim (167°C); His (280°C) and increases with the basic strength of the guest molecules.

A punctual discussion on the intercalation mechanism and the interlayer organization of the guest molecules must await a knowledge of the structure of the intercalates, and spectroscopic studies (IR, Raman) are needed to indicate the nature of the host-guest interactions. Nevertheless, the knowledge of the structure of the host, the composition and interlayer distance of the intercalation compounds, and the physico-chemical and structural features of the guest molecules allow us to put forward some considerations.

From the experimental results, it can be inferred that the general rule according to which mono- and bifunctional organic bases fully intercalated between the layers of $ZrPH_2$ arrange themselves as a bi- and monolayer, respectively, do not hold in the present case. In fact, the composition and the interlayer distance of the intercalation compounds with imidazole $ZrPH_20.8Im\ 1.33H_2O$ (10.9 Å) and benzimidazole $ZrPH_21.9Bim\ 1.5H_2O$ (20.4 Å), are in agreement with the presence of a monolayer and bilayer, respectively. In the case of histamine and histidine, both containing two basic functions – the first is intercalated as a bilayer in $ZrPH_21.9Him\ 2.2H_2O$ (20.5 Å) and the second as a monolayer in $ZrPH_20.9His\ 2H_2O$ (16.2 Å) or $ZrPH_{1.1}Na_{0.9}0.95His\ 2H_2O$ (15.1 Å).

The different behaviour of imidazole and benzimidazole may be explained on the basis of their steric and electronic effects and solvation requirements.

Imidazole is a relatively strong base with a marked hydrophilic and polarizing character and easily engages the N in position 1 in a hydrogen bond. Very likely, the strong electrostatic field associated with the relatively small, protonated imidazole molecules, lying as a monolayer in the interlayer region of $ZrPH_2$, hinders the intercalation of further base, and enhances the forces that hold the layers together. A high activation energy would thus be required to spread the layers apart in order to allow the accommodation of other imidazole molecules and the formation of the bilayer.

Benzimidazole, due to its hydrophobic and weaker basic character and the dielectric effect associated with the presence of the phenyl ring, can be arranged as a bilayer. In such an arrangement, the hydrophobic interactions between the phenyl group are enhanced since, in each layer, the molecules are forced to be oriented, parallel to each other, in an upright position with the N of the imidazole ring contained in the half cavity formed by the hexagonal arrangement of the —POH groups on the surface of the sheet of $ZrPH_2$. The distance between the half cavities, 5.3 Å, allows the accommodation of a benzimidazole molecule (having a van der Waals thickness of 3.7 Å) for each half cavity, and does not permit the interpenetration of the benzimidazole guests interacting with the P—OH groups belonging to two facing layers. Similar arguments can be invoked to also explain the known intercalation behaviour of pyridine and aniline, which for some aspects (basicity, solvation, aromatic character) form a pair of molecules similar to imidazole and benzimidazole, respectively. In fact, pyridine [14] gives rise to a monolayer ($ZrPH_20.45Py \cdot H_2O$ (10.9 Å)) as does imidazole, but aniline [15] forms a bilayer ($ZrPH_2 \cdot 2An \cdot H_2O$ (18 Å)) as benzimidazole.

Histamine behaves as an alkyl monoamine and gives an intercalation compound having an interlayer distance (20.5 Å) very near to that found [15] in the *n*-pentylmonoamine-zirconium phosphate complex ($ZrPH_2 \cdot 2Pe \cdot H_2O$ (21.5 Å)). It may be thought that histamine is arranged as a bilayer of extended molecules having the aliphatic $-NH_2$ group protonated by the P—OH of the host and the longer axis inclined by an angle of $\sim 60°$ with respect to the sheets (this arrangement should be favoured by the hydrophobic character of the aliphatic chains). In the absence of steric hindrance, such an interlayer organization would be much more stable than that arising from the presence of a monolayer of histamine having the $-NH_2$ protonated by a phosphate group and the weaker basic N of the imidazole ring interacting with another P—OH group.

Histidine, owing to the presence of the Zwitter ion that weakens the basic strength of the $-NH_2$ group and the steric hindrance of the $-COOH$ group towards the approach to the other guest molecules, involves the arrangement as a monolayer.

Another interesting feature of the present work arises from the analysis of the sequence of the steps of intercalation that lead to the phases with higher content of guest species. The sequences are not related to the pK_a values of the heterocyclic bases and do not follow those of a regular and progressive saturation of the P—OH groups present in the interlayer region (e.g., 1 by 2 or 1 by 4 and so on). It may be observed that in their first step of intercalation imidazole, benzimidazole and histamine give phases having an interlayer distance ranging between 10.6 and 11.3 Å. The increment, when referred to the interlayer distance of $ZrPH_2$ (7.6 Å), is consistent with the presence of a monolayer of molecules lying parallel, or nearly parallel, to the layers of the host structure. Figure 6 schematically shows such an arrangement for these guests. Since each molecule, interacting with a —P—OH group, gives a different covering of adjacent active sites, the intercalation compound having an interlayer distance of *ca.* 10.8 Å will have a composition related to the van der Waals planar dimension of the guest, as indeed is found. When other molecules are forced to enter the interlayer region, the guests would arrange themselves in more slanted positions according to their size and the hexagonal disposition and density of the P—OH groups in the interlayer region. It seemed of interest to estimate how much of the interlayer volume created by the expansion of the basal interlayer spacing is filled by the guest molecules for each of the examined intercalation compounds. With reference to one square centimetre of layer, the interlayer volume (V_i) is simply given by $\Delta d \times 10^{16}$ Å^3, where Δd is obtained by subtracting the thickness of the $ZrPH_2$ sheet (considered equal to 7.6 Å) from the experimental value of the interlayer distance of the intercalation compounds. A rough estimate of the volume occupied by the guest molecules

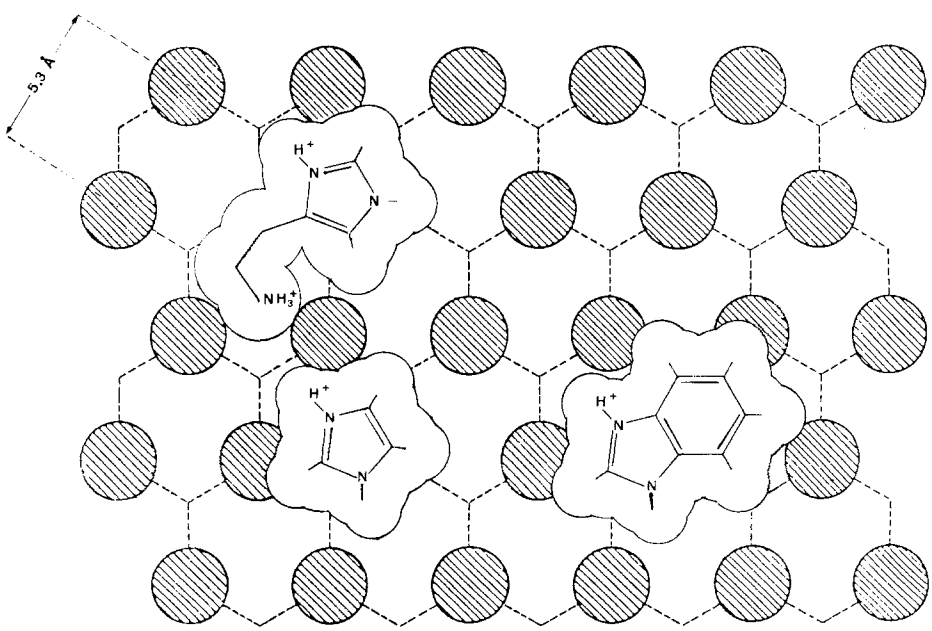


Fig. 6. Idealized representation of imidazole, benzimidazole and histamine molecules lying flat in the interlayer region of α-$[Zr(PO_4)_2]H_2 \cdot H_2O$. The dashed circles represent the —OH groups present on one side of the sheet.

(V_m) may be obtained by multiplying the van der Waals volume of each molecule by the number of molecules present in 1 cm^2 of layer. This number is, in turn, simply obtained by multiplying the mol of guest per mol of $ZrPH_2$ by 4.12×10^{14}, which is the number of —P—OH groups present in a square centimetre of layer.

The van der Waals volume of each guest molecule has been derived from the known unit-cell dimensions of crystalline imidazole [16], benzimidazole [17], histamine [18] and *L*-histidine [19]. The volume of each guest molecule was taken to be equal to the unit-cell volume divided by the number of molecules contained in the unit-cell, neglecting the molecular packing coefficient in the crystals.

Table V. Ratio between the van der Waals volume of the intercalated guests (V_m) and the interlayer volume (V_i) for the various intercalation compounds. The van der Waals volume of each guest has been assumed to be: Imidazole: 90 $Å^3$; Benzimidazole: 159 $Å^3$; Histamine: 152 $Å^3$; Histidine: 178 $Å^3$ (see text).

Intercalation compounds	V_m (10^{16} $Å^3$)	V_i (10^{16} $Å^3$)	V_m/V_i
$ZrPH_2$0.8Im .33H_2O	3.0	3.3	0.91
$ZrPH_2$0.75Bim 2.25H_2O	4.9	6.0	0.82
$ZrPH_2$1.4Bim 2.1H_2O	9.2	11.1	0.83
$ZrPH_2$1.9Bim 1.5H_2O	12.4	12.8	0.96
$ZrPH_2$0.33Him 1.65H_2O	2.1	3.0	0.70
$ZrPH_2$0.67Him 2.1H_2O	4.2	5.3	0.79
$ZrPH_2$1Him 2.1H_2O	6.3	7.1	0.89
$ZrPH_2$1.9Him 2.2H_2O	12.4	12.9	0.96
$ZrPH_2$0.5His 2H_2O	3.7	4.7	0.79
$ZrPH_2$0.9His 2H_2O	6.6	8.6	0.77
$ZrPH_{1.85}Na_{0.15}$0.17His 2H_2O	1.3	1.8	0.72
$ZrPH_{1.9}Na_{0.1}$0.66His 2H_2O	4.9	5.7	0.86
$ZrPH_{1.1}Na_{0.9}$0.95His 2H_2O	7.0	7.5	0.93

Table V reports, for each of the listed intercalation compounds, the volume of the guests, V_m, the interlayer volume, V_i, and their ratio. The volume filled by cointercalated water molecules has been neglected. It is very likely that the water molecules are in the half cavities formed by the hexagonal arrangement of the —P—OH groups present on each side of the sheet and their volume is partially accounted for by the assumption that the $ZrPH_2$ sheet has a thickness of 7.6 Å.

It may be seen from Table V that the ratio V_m/V_i is greater than 0.7 and it reaches a value close to 1 when a double layer of intercalated molecules is present in the interlayer region (0.96 for $ZrPH_2$1.9Bim and for $ZrPH_2$1.9Him). It may be noted that when the ratio V_m/V_i is equal to 1, the intercalated molecules will have a packing density between the sheets equal to that of the molecules in the crystalline state. It seems that in each of the intercalation compounds, the interlayer distance is kept to a minimum value, which permits a maximum packing of the intercalated guests. This packing, in turn, will depend on the shape of the guest and the different conformation that it may assume in the interlayer region. With this in mind, it is not easy to foresee the sequence of the steps that lead to the full intercalation of a given guest, especially when it is a rather complex species. In the present case, it is particularly

difficult to speculate on the arrangement of histidine between the layers. Again, structural studies will help to elucidate such conformations.

In a recent paper, Solin [20] has attracted the attention of researchers interested in the solid state physics and chemistry of layered materials, to some clay intercalation compounds whose structure may be solved by the method of profile fitting of the X-ray powder diffractograms, a technique which is more frequently used for the study of graphite or layered dichalcogenide intercalation compounds. It is hoped that attention will also be devoted to layered insoluble acid salts, and in particular to α-zirconium phosphate which offers the advantage of having a structure much more complex than that of graphite and much more regular than that of the most common clays.

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