

Intercalates of α -Sn(HPO₄)₂·H₂O with Aromatic and Heterocyclic Bases and Some Comments on Their Orientation in the Interlayer Region

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Abstract. The intercalation of amines into α -tin(IV) hydrogen phosphate, α -Sn(HPO₄)₂·H₂O, (α -SnP) can occur to give mono- or bilayers of the guest molecule. The distribution and orientation of the amines is influenced by geometrical factors, acidity of the guest molecule and moreover, the degree of charge localisation of the guest organic cations. Regarding the monolayer formation, there are two possibilities. The first is that aromatic amines form monolayers with parallel orientation of the amine with respect to the phosphate layer, when the charge is delocalised over the aromatic ring. Monolayer formation with perpendicular orientation occurs when the positive charge is localised in opposite parts of the aromatic ring molecule. Bilayer formation occurs when the positive charge is localised in one part of the molecule and simultaneous interaction with two adjacent layers is not possible.

Key words. α -Sn(HPO₄)₂·H₂O, intercalation, molecular orientation, amines.

1. Introduction

A vast intercalation chemistry of layered compounds, particularly clays and M(IV) hydrogen phosphates, has been developed in recent years [1, 2]. The layers of clays (smectites, vermiculites, etc.) are negatively charged as a consequence of isomorphic substitution in the crystal framework. The layer charge of such compounds is compensated by inorganic or organic cations, producing a modification of the crystallographic parameter *c* of the host lattices. A different situation occurs in the case of M(IV) hydrogen phosphates, where the layers are not initially charged, and where acid P—O—H groups are responsible for the ion exchange and intercalation properties. The cationic exchange capacity (CEC) of such compounds is 4–6 times higher than those of clays. The extent of intercalation of organic cations in clays appears to be dependent on the layer charge density. Available data [3] indicate that, when charge density increases, so does the inclination of the organic cation with respect to the layers ($\alpha = 0^\circ$ – 90°). Organic cations forming monolayers or bilayers give the largest possible interaction with the host matrix. With respect to α -SnP, a lamellar microcrystalline solid, amine uptake is not always

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correlated to the pK_a of the guest molecule. Primary alkylamines ($pK_a \geq 9$) are sufficiently basic to react with all available protons up to the CEC. Bilayers are formed in which the alkyl chains are inclined at 60° with respect to the layers [4]. The covering effect impedes however the intercalation of basic molecules, such as piperidine ($pK_a = 11.12$) up to the limit of the CEC in the phosphate [5]. In this case, the most effective possible interaction of piperidine molecules with the phosphate requires the expansion of the phosphate layers to form organic bilayers, which are oriented at 60° to the layer plane [5]. For amines of intermediate base strength ($9 \geq pK_a \geq 4.5$), the orientation of the organic molecules can vary considerably and no correlation with pK_a is found. For example, aniline ($pK_a = 4.6$) forms bilayers ($\alpha = 60^\circ$) with 100% of the CEC neutralized, whereas pyridine ($pK_a = 5.25$), which is more basic than aniline, adopts a flat disposition with only 25% of the CEC neutralized. The orientation of the guest molecules, therefore critically influences the effective intercalation capacity of the phosphate. Further complications arise when organic molecules have two basic groups, as with aromatic diamines and aminopyridines [6]. Clearly, both acid-base and geometrical factors are not the only considerations involved in determining the orientation of the intercalated molecules in α -SnP. Using previous and new data, some considerations about the orientation of the basic guest molecules within the interlayers of α -tin phosphate are made in this work.

2. Experimental

All the chemicals were of reagent grade and were used without further purification. Preparations of α -SnP and its intercalation compounds with *n*-alkylamines, piperidine, pyridine, 4,4'-bipyridine, aniline, *m*-toluidine, 3,5-dimethylaniline, benzidine, 2-amino-4-methylpyridine, *o*-, *m*-, and *p*-phenylenediamine were as described elsewhere [4–6].

Intercalation of 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, imidazole, α -picoline, β -picoline and γ -picoline were achieved by adding an aqueous solution of the amine to an aqueous suspension of α -SnP in a Teflon sealed bottle at room temperature, for two days. The amine: α -SnP ratio ranged from 1:1 to 7:1. The solids were separated by centrifugation and washed several times with water. They were dried in a dessicator over 50% H_2SO_4 to eliminate surface adsorbed amines. Intercalation of methyl viologen was achieved by adding an aqueous suspension of its chloride salt to a suspension of $Sn(C_4H_{11}N)_2(HPO_4)_2 \cdot H_2O$, the *n*-butylammonium- α -SnP intercalation compound, (molar ratio methyl viologen: *n*-butylammonium- α -SnP = 7:1) at $50^\circ C$; the solid was washed and dried as described above. A new procedure to intercalate pyridinium using pyridinium chloride was carried out by adding an aqueous solution of the salt to an aqueous suspension of $SnNMe_4H(PO_4)_2 \cdot n H_2O$ (molar ratio pyridinium : $SnNMe_4H(PO_4)_2 \cdot H_2O = 6:1$) [7].

The intercalation compounds were characterised by chemical analysis, X-ray diffraction (XRD), infrared spectroscopy (IR), and differential and thermogravimetric analyses (DTA-TG). The XRD patterns were recorded on a Siemens D500 diffractometer using monochromatic CuK_α radiation, least squares unit cell refinement with indexing was done with the program LSCUCR-87 [8]. DTA-TG analyses

were carried out on a Rigaku thermoflex using calcined Al₂O₃ as the internal standard reference and 10 K/min as a heating rate. In all cases TG and CHN analyses were in good agreement. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer using the KBr disc method.

3. Results and Discussion

The intercalation of all amines occurred by means of an acid base topotactic reaction between the layered acid phosphate and the basic amines. For the case of methyl viologen, however, the *n*-butylammonium- α -SnP intercalation compound was used. Tables I–IV show the composition, crystallographic parameters and interlayer distances of the intercalation compounds. The powder XRD patterns of the intercalates can be indexed on the basis of monoclinic unit cells. In all cases, the *a* and *b* constants are very similar to those of α -SnP (*a* = 8.61 Å, *b* = 5.02 Å). The absence of *hkl* lines, where *h* + *k* ≠ 2*n*, suggested the retention of the *n*-glide plane of the phosphate. The data indicated that the layered structures have been preserved but that the interlamellar spaces have expanded (Tables II, IV). According to the values of the crystallographic parameters *a* and *b*, the free area per active site is 21.6 Å² [9].

3.1. MONOLAYER FORMATION OF PLANAR MOLECULES WITH PARALLEL ORIENTATION

In α -, β - and γ -picolines, the presence of the methyl group results in a slight increase in the basicity of the heterocyclic nitrogen in comparison with pyridine. Intercalation of such molecules occurs through an acid base reaction with protonation of the nitrogen, and this has been confirmed by the appearance of a band at 1545 cm⁻¹ which corresponds to δ NH⁺ in the IR spectra of all the picoline- α -SnP intercalation compounds. There is a correlation between the observed composition and the basicity of picolines. However, only up to 25% of the lamellar protons are neutralised. The basal spacings of the intercalates containing α -, β - and γ -picolines are 11.7, 11.2 and 12.9 Å respectively. Taking into account the area covered by a picoline molecule, the maximum capacity with this orientation is 20% of the CEC. Interlayer distance and composition data of the α - and γ -picoline intercalates point to a slightly slanted position of such molecules ($\approx 30^\circ$) and some interpenetration of the nitrogen between the phosphate layers, whereas β -picoline would lie flat, as the basal spacing of the intercalate is nearly the sum of the *d*₀₀₂ of α -SnP plus the van der Waals thickness of the aromatic ring. The positive charge is delocalised along the aromatic ring in all the picolines, and hence the strongest interaction with the negative charge of the layer occurs with a parallel or almost parallel disposition of the aromatic ring (Figure 1). This behaviour has been observed in the case of pyridine [5].

3-Aminopyridine is a basic molecule with a single p*K*_a value of 6.03. The observed maximum composition of the intercalate is 0.47 mol amine per mol of α -SnP (23% neutralization) and the interlayer distance is 11.95 Å. These values are similar to those observed with picolines which possess analogous van der Waals areas and basicity, and thus, a parallel disposition of the aromatic ring with respect

Table I. Composition of pyridine and pyridine derivatives- α -SnP intercalation compounds from elemental chemical analysis and thermogravimetric analysis.

Intercalated amine	Mol amine added: mol α -SnP	Observed			Calculated			Formula	Ref.
		C	H	N	C	H	N		
Pyridine	7:1	6.80	1.70	1.60	6.81	1.68	1.59	Sn(C ₅ H ₅ N) _{0.41} (HPO ₄) ₂ ·H ₂ O	5
4,4'-Bipyridine	6:1	8.14	1.61	1.93	8.16	1.63	1.90	Sn(C ₁₀ H ₈ N ₂) _{0.25} (HPO ₄) ₂ ·H ₂ O	5
2-Aminopyridine	7:1	12.71	2.28	5.80	12.60	2.24	5.88	Sn(C ₅ H ₆ N ₂) _{0.86} (HPO ₄) ₂ ·H ₂ O	*
3-Aminopyridine	4:1	7.22	1.78	3.40	7.56	1.83	3.53	Sn(C ₅ H ₆ N ₂) _{0.47} (HPO ₄) ₂ ·H ₂ O	*
4-Aminopyridine	4:1	11.07	2.11	5.30	10.98	2.23	5.41	Sn(C ₅ H ₆ N ₂) _{0.72} (HPO ₄) ₂ ·H ₂ O	*
2-Amino-4-methylpyridine	7:1	20.28	3.48	8.32	20.90	3.15	8.13	Sn(C ₆ H ₈ N ₂) _{1.39} (HPO ₄) ₂ ·0.5H ₂ O	6
α -Picoline	2:1	8.93	2.05	3.40	8.87	2.17	3.45	Sn(C ₆ H ₇ N) _{0.47} (HPO ₄) ₂ ·1.5H ₂ O	*
β -Picoline	2:1	7.61	2.20	2.91	7.50	2.29	2.92	Sn(C ₆ H ₇ N) _{0.40} (HPO ₄) ₂ ·2H ₂ O	*
γ -Picoline	2:1	9.30	2.15	3.48	9.21	2.20	3.58	Sn(C ₆ H ₇ N) _{0.49} (HPO ₄) ₂ ·1.5H ₂ O	*
Methyl viologen	3:1	8.51	1.98	1.72	8.57	1.92	1.67	Sn(C ₁₂ H ₁₄ N ₂) _{0.22} (HPO ₄) ₂ ·H ₂ O	*

*This work

Table II. Crystallographic parameters, interlayer distances, and pK_a values of pyridine and pyridine derivatives- α -SnP intercalation compounds.

Intercalated amine	Crystallographic parameters				d_{002} (Å)	pK_a	Ref.
	a (Å)	b (Å)	c (Å)	β (°)			
Pyridine	8.60	4.98	24.46	110.0	11.48	5.25	5
4,4'-Bipyridine	8.68	4.94	24.80	97.6	12.43	-	5
2-Aminopyridine	8.55	4.98	26.30	103.3	12.60	6.71	*
3-Aminopyridine	8.60	5.00	24.30	98.1	11.95	6.03	*
4-Aminopyridine	8.59	5.02	25.40	97.8	12.45	9.11	*
2-Amino-4-methylpyridine	8.50	4.98	37.54	99.5	18.50	-	6
α -Picoline	8.57	4.99	24.60	110.2	11.70	5.94	*
β -Picoline	8.60	5.02	23.80	110.0	11.22	5.63	*
γ -Picoline	8.60	5.00	26.82	105.1	12.90	6.03	*
Methyl viologen	8.65	4.95	25.00	98.0	12.60	-	*

*This work

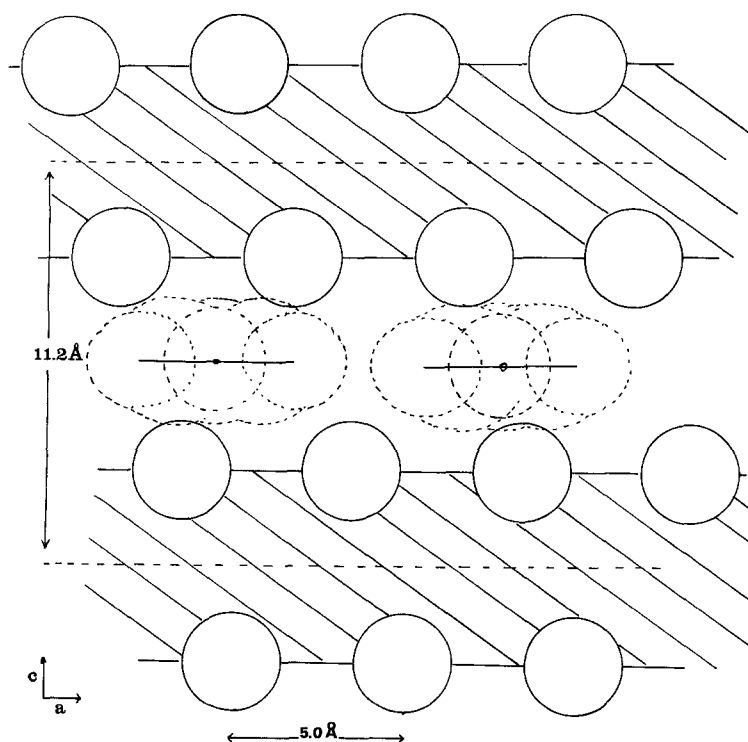
Fig. 1. Scale drawing of the β -picoline- α -tin(IV) hydrogen phosphate intercalate (projection of the plane ac). The open circles are $-\text{OH}$ groups of $\text{O}_3\text{P}-\text{OH}$.

Table III. Composition of some amine- α -SnP intercalation compounds from elemental analysis and thermogravimetric analysis.

Intercalated amine	Mol amine added: mol α -SnP	Observed			Calculated			Formula	Ref.
		C	H	N	C	H	N		
Aniline	6:1	28.04	3.48	5.41	27.98	3.50	5.44	$\text{Sn}(\text{C}_6\text{H}_7\text{N})_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	5
<i>m</i> -Toluidine	6:1	31.03	4.00	5.13	30.96	4.05	5.16	$\text{Sn}(\text{C}_7\text{H}_9\text{N})_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	5
3,5-Dimethylaniline	6:1	26.98	4.15	3.89	26.91	4.16	3.93	$\text{Sn}(\text{C}_8\text{H}_{11}\text{N})_{1.4}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	5
Benzidine	5:1	29.85	2.41	5.80	28.08	2.34	5.46	$\text{Sn}(\text{C}_{12}\text{H}_{12}\text{N}_2)_{1.07}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	6
<i>o</i> -Phenylenediamine	5:1	22.48	3.54	8.66	22.40	3.30	8.71	$\text{Sn}(\text{C}_6\text{H}_8\text{N}_2)_{1.54}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	6
<i>m</i> -Phenylenediamine	5:1	14.19	2.78	5.53	14.15	2.53	5.50	$\text{Sn}(\text{C}_6\text{H}_8\text{N}_2)_{0.74}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	6
<i>p</i> -Phenylenediamine	3:1	21.61	3.20	8.41	21.62	3.22	8.41	$\text{Sn}(\text{C}_6\text{H}_8\text{N}_2)_{1.46}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	6
Imidazole	2:1	8.80	1.95	5.80	8.77	1.99	5.85	$\text{Sn}(\text{C}_3\text{H}_4\text{N}_2)_{0.96}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	*
Ethylenediamine	2:1	6.23	3.01	7.21	6.19	3.09	7.22	$\text{Sn}(\text{C}_2\text{H}_6\text{N}_2)_{1.0}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	*
Piperidine	6:1	17.65	4.40	4.01	17.58	4.43	4.10	$\text{Sn}(\text{C}_5\text{H}_{11}\text{N})_{1.26}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	5

*This work

to the layers would be expected. The positive charge originated by protonation is delocalised along the aromatic ring again, but not in the case of 2- and 4-aminopyridine. To confirm the hypothesis that protonated pyridine and its derivatives, with the positive charge delocalised along the aromatic ring, are intercalated into α -SnP with a parallel disposition with respect to the layer, the intercalation of methyl viologen was studied. This bicyclic molecule was intercalated by ion exchange into the phosphate using the *n*-butylammonium- α -SnP intercalation compound as precursor [10, 11]. The theoretical maximum uptake of 1 mol of methyl viologen per mol of α -SnP was not attained, only 0.22 mol of methyl viologen per mol of α -SnP was obtained (11% neutralisation). Elemental analysis and IR spectroscopic data indicate the absence of *n*-butylammonium ions in the solid. The interlayer distance ($d_{002} = 12.6 \text{ \AA}$) and the composition agree with a parallel disposition of the molecule with its rings twisted at 45° , covering a surface area of 88 \AA^2 . These results are similar to those observed in the intercalation of 4,4'-bipyridine into α -SnP, where the interlayer distance is 12.43 \AA and the composition is 0.25 mol of amine per mol of α -SnP [5].

The formation of a pyridinium ion with a parallel disposition of the ring to the layer was also observed in the study of the intercalation of neutral pyridine using several solvents [5]. An attempt to obtain a pyridine- α -SnP intercalation compound with a different pyridine orientation failed. The pyridine intercalation compound was obtained by ion exchanging the pyridinium ion (pyridinium chloride) with the half exchanged tetramethylammonium tin phosphate phase, Sn-NMe₄H(PO₄)₂·H₂O, an excellent intercalating precursor [7]. In this experiment a similar composition and interlayer distance was obtained as in the case of the intercalation of neutral pyridine. This means that the observed composition and disposition are independent of the intercalation mechanism (acid-base reaction and ion exchange reaction), and that these are functions of the strength of acid sites and the delocalisation of the positive charge.

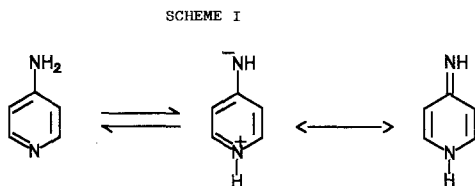
Table IV. Crystallographic parameters, interlayer distances and pK_a values of some amine- α -SnP intercalation compounds.

Intercalated amine	Crystallographic parameters				d_{002} (Å)	pK_{a1}	pK_{a2}	Ref.
	a (Å)	b (Å)	c (Å)	β (°)				
Aniline	8.56	5.06	38.72	98.5	19.07	4.60		5
<i>m</i> -Toluidine	8.60	5.04	38.80	96.1	19.20	4.70		5
3,5-Dimethylaniline	8.65	5.01	39.33	93.7	19.50	4.91		5
Benzidine	8.54	4.96	35.55	97.1	17.92	4.97	3.75	6
<i>o</i> -Phenylenediamine	8.50	4.98	37.94	98.7	18.90	4.74	0.60	6
<i>m</i> -Phenylenediamine	8.56	4.96	27.03	104.5	13.10	4.98	2.41	6
<i>p</i> -Phenylenediamine	8.50	5.03	27.91	104.4	13.50	6.20	2.67	6
Imidazole	8.50	5.01	22.30	97.20	10.92	6.95		*
Ethylenediamine	8.56	5.02	22.10	101.2	10.80	10.71	7.56	*
Piperidine	8.58	5.00	32.80	107.0	15.70	11.12		5

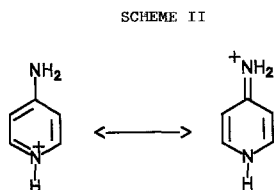
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3.2. MONOLAYER FORMATION WITH VERTICAL DISPOSITION

4-Aminopyridine is a molecule that has the following tautomeric equilibria:



The position of the NH_2 groups results in a great increase in the basic power ($\text{p}K_a = 9.11$) and only a proton can be accepted. The more important canonical forms of the protonated species are [12].



The localisation of the positive charge at the end of the C_2 molecular axis permits a simultaneous interaction with two adjacent layers of the phosphate. The interlayer distance of the intercalation compound (12.45 Å) is comparable to that observed in the *p*-phenylenediamine- α -SnP intercalate (13.5 Å) where monoprotonation also occurs [6] and the C_2 molecular axis is almost perpendicular to the layer (Figure 2).

Composition data also support this orientation, but the monolayer is not completed. The IR spectrum shows bands at 1660 and 1530 cm^{-1} , the former attributed to the increase in aliphatic character of the $\text{C}=\text{NH}_2^+$ bond, and the latter to the pyridinium ion (Figure 3). An analogous behaviour in the case of *m*-phenylenediamine was also observed [6].

2-Aminopyridine is intercalated into α -SnP forming a monolayer of aromatic rings perpendicularly oriented to the layers. This is supported by the interlayer distance (12.6 Å) and the composition (0.86 mol amine per mol of α -SnP). In this case, the positive charge is localised in two opposite parts of the molecule: between the two nitrogen atoms and on the γ carbon, which presents a positive partial charge (δ^+) [12]. This permits a simultaneous interaction of the organic molecule with two adjacent phosphate layers. The IR spectrum of this intercalation compound (Figure 3) shows a band at 1547 cm^{-1} assigned to a vibrational mode of the pyridinium ion. The strong band at 1664 cm^{-1} is assigned to the $\nu(\text{C}=\text{N}^+)$ aliphatic bond. In the case of 2-amino-4-methylpyridine the existence of a hydrophobic methyl group bonded to the γ carbon eliminates the possibility of the simultaneous interaction with two layers, and the energy involved in the process is sufficient to swell the layers giving rise to the formation of bilayers.

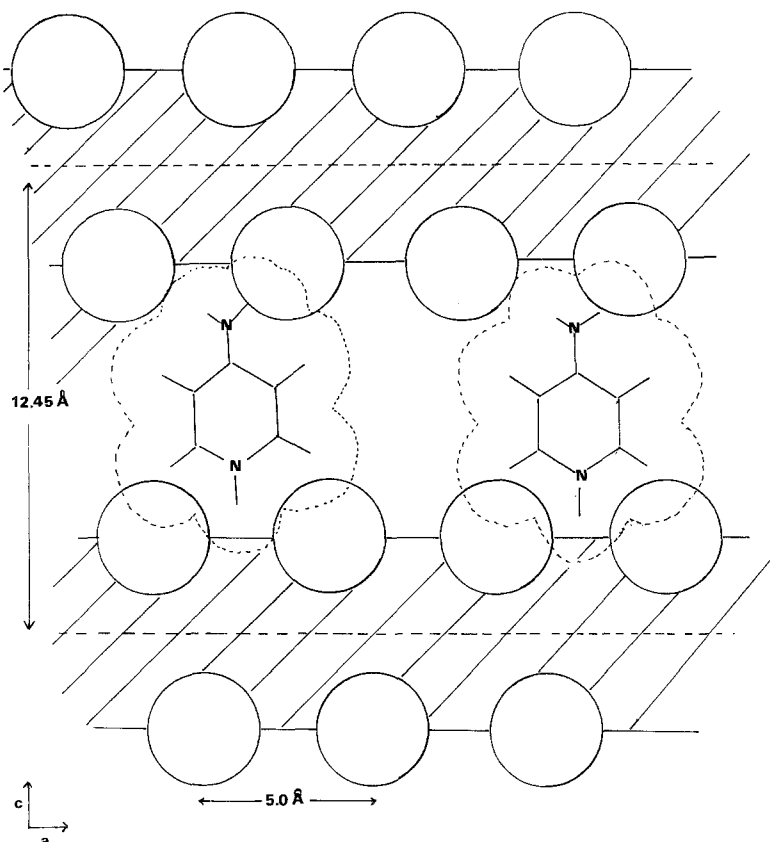
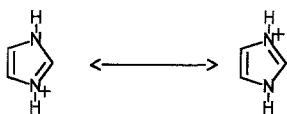


Fig. 2. Scale drawing of the 4-aminopyridine- α -tin(IV) hydrogen phosphate intercalate (projection of the plane ac).

The intercalation of imidazole results in the formation of a monolayer. Although imidazole can only accept a proton, protonated imidazole has the positive charge mainly localised in both heterocyclic nitrogens. The composition is close to 1 mol of imidazole per mol of α -SnP. Inasmuch as the positive charge is not delocalized along the aromatic ring, a parallel disposition of the ring cannot be supported by the composition data (0.96 mol imidazole per mol of α -SnP); a slanted position ($\alpha \sim 50^\circ$) of the imidazole ring is suggested according to the basal spacing found (10.92 Å). This disposition allows a simultaneous interaction of both —NH groups of the aromatic ring with two adjacent layers.

SCHEME III



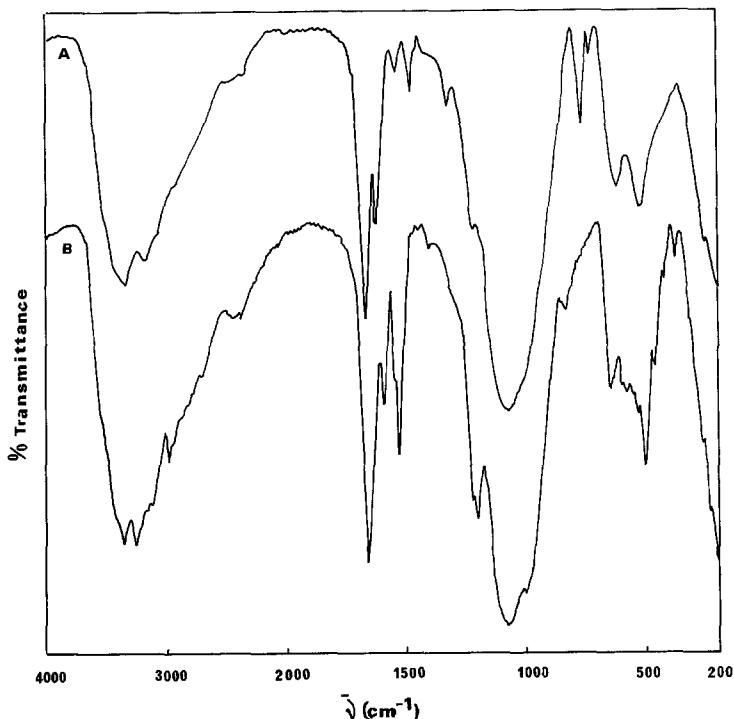


Fig. 3. IR spectra of (A) the 2-aminopyridine- α -SnP intercalation compound, (B) the 4-aminopyridine- α -SnP intercalation compound (in cm⁻¹).

When the intercalated molecules possess two strongly basic terminal groups biprotonation is possible and thus they tend to orientate completely vertical. This occurs with benzidine [6].

3.3. BILAYER FORMATION

When the positive charge of a monoprotonated species that also possesses hydrophobic groups is localised in a part of the molecule, bilayer formation with alkyl or aryl residues inclined with respect to the layers must be expected in the intercalation compounds with α -SnP. The nitrogen interacts with the H—O—P group and hydrophobic groups overlap. In effect, the intercalation of aniline, *m*-toluidine, 3,5-dimethylaniline, 2-amino-4-methylpyridine, *o*-phenylenediamine, piperidine (Tables II, IV) and alkylamines gives rise to bilayers with the molecules inclined 60° with respect to the layers as reported [4–6].

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