High-resolution solid-state magic angle spinning nuclear magnetic resonance studies on the layered antimony hydrogen phosphate, $HSb(PO_4)_2{\cdot}2H_2O$, and its reaction products with tetrakis(pyridyl)iron(II) chloride

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The antimony hydrogen phosphate, $HSb(PO_4)_2{\cdot}2H_2O$ (denoted $H_1SbP_2{\cdot}2H_2O$), has been synthesised *via* the ion exchange of crystalline $KSb(PO_4)_2$, (K_1SbP_2), with 9 M HNO_3. Scanning electron microscopy (SEM) confirmed that the crystalline K_1SbP_2 was formed by the so-called 'deck of cards' mechanism to give randomly orientated lamellae. The synthesised $H_1SbP_2{\cdot}2H_2O$ host material was studied using ^1H and ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) techniques. Intercalation studies were carried out using tetrakis(pyridyl)iron(II) chloride, $[Fe(py)_4Cl_2]{\cdot}H_2O$. The resulting products were analysed using powder X-ray diffraction (PXRD) and ^{31}P MAS NMR techniques. The former suggested that the $[Fe(py)_4Cl_2]{\cdot}H_2O$ complex lost its water of crystallisation during the reaction and did not intercalate in its intact state between adjacent layers of the $H_1SbP_2{\cdot}2H_2O$ crystallites. ^{31}P MAS NMR data suggested that the $H_1SbP_2{\cdot}2H_2O$–$[Fe(py)_4Cl_2]$ reaction products contained phosphorus resonances which could be assigned as belonging to (i) unaltered host $H_1SbP_2{\cdot}2H_2O$ (protonated) phosphate groups, (ii) phosphate groups bonded to the intercalating species. In addition, a separate, $Q_P{}^3$, resonance was also noted which was thought to arise from a chemically unaltered phosphate group of the host $H_1SbP_2{\cdot}2H_2O$ perturbed by the close proximity of the sorbed $[Fe(py)_4]^{2+}$ cationic species.

Recently, there has been renewed interest in the structure and properties of antimony hydrogen phosphates (or the so-called phosphatoantimonic acids) arising from their potential as cation exchangers for nuclear and non-nuclear industrial separation processes.[1] Secondary interest also arises from their increased use as strongly acidic catalyst supports which have found use within the petrochemical industry. The title antimony hydrogen phosphate, $HSb(PO_4)_2{\cdot}2H_2O$, is just one member of a series of acidic antimony hydrogen phosphates. The ideal composition of members of this series can be represented by $H_nSb_nP_2O_{(3n+5)}{\cdot}xH_2O$, where n is an odd integer, *e.g.* 1, 3, 5 …, and x is variable depending upon the degree of hydration of the phosphate.

The lower members of this series ($n=1$ or 3) have two-dimensional lattice structures.[2] In the case of the title compound in the present study, $HSb(PO_4)_2{\cdot}2H_2O$ (referred to hereafter as $H_1SbP_2{\cdot}2H_2O$ or antimony hydrogen phosphate), these layers are arranged in a series of infinite $[SbP_2O_8{}^-]_n$ sheets comprising SbO_6 edge-sharing octahedra and PO_4 tetrahedra, with each octahedron connected to six tetrahedra and each tetrahedron connected to three SbO_6 octahedra.[3,4] This structure, which is thought to be related to that of α-zirconium hydrogen phosphate,[5] is shown more clearly in Fig. 1.

The amount of water contained within the interlayer regions of the antimony hydrogen phosphate is extremely variable. In addition there is also a relatively large amount of surface sorbed water to be considered. The sensitivity of these compounds is demonstrated by a distinct swelling of the synthesised $H_1SbP_2{\cdot}2H_2O$ upon exposure to a normal laboratory atmosphere.[6]

In the present study it was decided to thoroughly investigate the structure of the phosphate groups in the antimonic acid, $H_1SbP_2{\cdot}2H_2O$, using both single-pulse (SP) and cross-polarisation (CP) ^{31}P high-resolution solid-state MAS NMR techniques. In addition, the technique of ^1H high-resolution solid-state MAS NMR was used to try and identify any changes occurring in the protonic species contained within the host antimonic acid after calcination at various temperatures.

Experimental

Materials

The synthesis of the $Sb_2O_5(s)$ precursor required $Sb_2O_3(s)$ and 30% mass/volume (m/v) $H_2O_2(aq)$, both of which were GPR grade and supplied by BDH Ltd. The synthesis of the crystalline K_1SbP_2 required the following: $NH_4H_2PO_4(s)$, $KH_2PO_4(s)$ and 16 M HNO_3 which were also supplied (as GPR reagents) by BDH Ltd. The synthesis of tetrakis(pyridyl)iron(II) chloride required iron powder (99.8+% purity) and pyridine (99+%) as supplied by Aldrich.

Preparation of $Sb_2O_5{\cdot}xH_2O$

Hydrated antimony pentaoxide, $Sb_2O_5{\cdot}xH_2O$, was prepared by heating Sb_2O_3 (100 g, 0.34 mol) in 30% m/v H_2O_2 solution

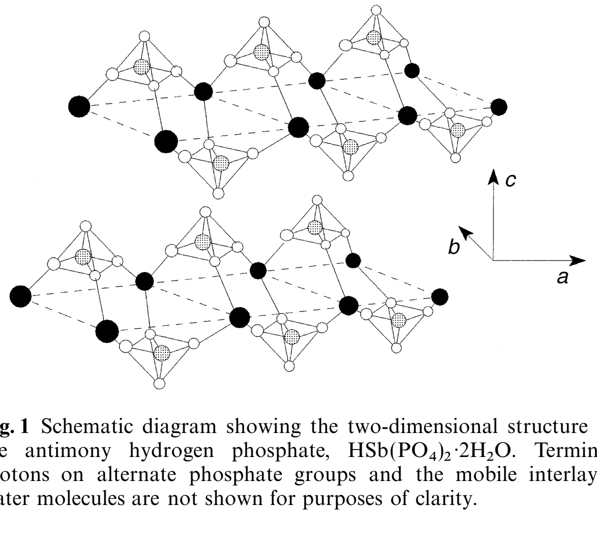

Fig. 1 Schematic diagram showing the two-dimensional structure of the antimony hydrogen phosphate, $HSb(PO_4)_2{\cdot}2H_2O$. Terminal protons on alternate phosphate groups and the mobile interlayer water molecules are not shown for purposes of clarity.

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(0.5 dm^{-3}) for 24 h at 80 °C. **CAUTION**: as mentioned in a previous paper,[1] the temperature must be carefully controlled because an exothermic reaction starts at *ca.* 50 °C which causes the temperature of the solution to rapidly rise to its boiling point.

The solution obtained by heating for 24 h was evaporated until the solid antimony pentaoxide precipitated. The oxide was then allowed to cool to room temperature whilst coming to equilibrium with the air. In particular, it was important to allow an equilibrium to be attained with the moisture in the laboratory atmosphere.

Preparation of the $HSb(PO_4)_2{\cdot}xH_2O$ ($x = ca.\ 2$) host

Preparation *via* crystalline $KSb(PO_4)_2$. The preparation of $H_1SbP_2{\cdot}2H_2O$ was carried out *via* the route suggested by Piffard *et al.*[2,4] Sb_2O_5(s), $NH_4H_2PO_4$(s) and KH_2PO_4(s) were intimately mixed in the stoichiometric ratio 0.5 : 1 : 1. The mixture was then heated in a platinum crucible using the following heating programme: (a) ambient temperature to 180 °C for 30 min, (b) 180 to 250 °C for 300 min, (c) 250 to 600 °C for 300 min and (d) holding at 600 °C for 240 min.

The powder was then cooled to room temperature, emptied from the platinum crucible and ground using an agate pestle and mortar and replaced in the crucible and heated according to the following heating programme: (e) ambient temperature to 900 °C for 300 min and (f) holding at 900 °C for 1800 min.

The crystalline $KSb(PO_4)_2$ thus produced was then ion exchanged using 9 M HNO_3 [100 cm^3 g^{-1} of $KSb(PO_4)_2$] at 50 °C for 24 h. The resultant solids containing the $H_1SbP_2{\cdot}2H_2O$ were then washed with aliquots of doubly deionised water [100 cm^3 g^{-1} of $H_1SbP_2{\cdot}2H_2O$] until free from nitrate anions. On average this usually took up to four washings. The gel produced was dried at 60 °C *in vacuo*. The water content of the H_1SbP_2 at ambient humidity varied between 1.8 and 2 mol of water per formula unit, although, on average, this was closer to 2 mol. Owing to the sensitivity of the material to changes in humidity it was necessary to store the $H_1SbP_2{\cdot}2H_2O$ in a dessicator with a 15 M H_2SO_4 atmosphere.

Preparation of $[Fe(py)_4Cl_2]{\cdot}H_2O$

Preparation of hydrated tetrakis(pyridyl)iron(II) chloride may be carried out by two different methods. The first relies upon the addition of $FeCl_2$(s) in anhydrous methanol to pure pyridine.[7] Although relatively quick, this method suffers from the major disadvantage of decomposition of the complex upon recrystallisation. It was, therefore, decided to use the second, but more time consuming, method below.[8]

Pure iron powder (5 g, 0.09 mol) was added carefully over a period of *ca.* 45 min to 15 cm^3 of 5 M hydrochloric acid. [**CAUTION**: large amounts of H_2(g) are evolved upon addition of the HCl and care should be exercised]. When all the H_2(g) was evolved, 20 cm^3 of sodium-dried methanol were added and the solution was filtered into a flask containing 100 cm^3 of pyridine (purified by distillation in a dry nitrogen atmosphere prior to use) under dry nitrogen. Intensely yellow crystals of tetrakis(pyridyl)iron(II) chloride separated out immediately from the solution. The flask was allowed to stand overnight under a dry N_2(g) atmosphere, then the crystals were filtered off, recrystallised from pure (distilled) pyridine and dried in a vacuum desiccator. The crystals were stored, ready for use, in sealed sample tubes under a nitrogen atmosphere. Since the crystals were light-sensitive it was also necessary to completely cover the outside of each sample tube with aluminium foil. This precaution enabled the crystals to remain stable when stored for several months.[9]

Intercalation experiments

Reaction of $H_1SbP_2{\cdot}2H_2O$ with tetrakis(pyridyl)iron(II) chloride. To tetrakis(pyridyl)iron(II) chloride (5 g, 2.23 × 10^{-2} mol) dissolved in redistilled pyridine under a dry nitrogen atmosphere was added $H_1SbP_2{\cdot}2H_2O$ (1 g, 2.86 × 10^{-3} mol) and the solution was refluxed for 30 min. After this time, the pale yellow solid formed was filtered off. The solid was then added to a fresh solution of $[Fe(py)_4Cl_2]{\cdot}H_2O$ in pyridine and stirred for a further 30 min. The remaining solid was then filtered off and dried in a vacuum oven at 40 °C for 18 h. The pale yellow solid obtained was then analysed by PXRD, MAS NMR and FTIR techniques.

Physical measurements. X-Ray powder diffraction data were collected on a Spectrolab Series 3000 CPS-120 diffractometer using Cu-Kα radiation ($\lambda = 1.540\,59$ Å). Samples were run on a plate orientated at an angle of 3–5°. Typical accumulation times for each powder pattern were in the range 650–700 s. FTIR spectra were recorded on a Perkin-Elmer 1720-X FTIR spectrometer with an IRDM data management system. All samples were run as 13 mm dry KBr discs with a ratio of sample to KBr of 1 : 100 by mass.[10]

Analysis. The ^{31}P MAS NMR spectra were run by the EPSRC Solid-state NMR Service at the University of Durham. All samples were run on a Varian VXR 300 spectrometer fitted with a Doty Scientific standard MAS probe (rotor outside diameter 7 mm, maximum sample volume 300 μl) and an Oxford Instruments 7.05 T superconducting magnet. Both single-pulse excitation and cross-polarised ^{31}P spectra were obtained at 121.4 MHz. All single-pulse and cross-polarised NMR spectra were run using magic angle spinning. All ^{31}P NMR spectra were referenced to 80% H_3PO_4.

The ^{1}H MAS NMR spectra were obtained at 299.95 MHz with a relaxation delay of 0.5 s. The spectra were referenced to tetramethylsilane.

Unfortunately, elemental analyses were not possible on either the synthesised $H_1SbP_2{\cdot}2H_2O$ or its reaction products. Our results indicate that the material, as synthesised, is resistant to both acid attack and concentrated base solution. Attempts to dissolve the materials in *aqua regia* and hydrofluoric acids were unsuccessful. Analyses of the water washings obtained during the pH adjustment of the $H_1SbP_2{\cdot}2H_2O$ indicated the absence of antimony.[11]

Results and Discussion

Formation of K_1SbP_2 and $H_1SbP_2{\cdot}2H_2O$: the 'deck of cards' mechanism

The formation of the antimonic acid was thought to occur *via* the so-called 'deck of cards' mechanism. This process involves the formation of individual lamellae which then join together to produce a structure similar to that of a randomly orientated deck of playing cards. The morphology of the antimonic acid salt (K_1SbP_2) produced by precipitation from solution is clearly illustrated by the scanning electron micrograph shown in Fig. 2. This structure is similar to that formed by amine intercalated tin hydrogen phosphate, α-$Sn^{IV}(HPO_4)_2{\cdot}H_2O$, and gives rise to the so-called 'end-site' particle interactions.[12] Such structures are thought to exist with areas of microporosity between individual lamellae (labelled A in the micrograph) and areas of mesoporosity between groups of lamellae (labelled B).

The changes to the K_1SbP_2 lamellae caused by acid etching during the K^+–H^+ ion exchange process are visible in the scanning electron micrograph of $H_1SbP_2{\cdot}2H_2O$ shown in Fig. 3 (which is taken at a lower magnification than Fig. 2). This clearly shows the effective delamination of individual lamellae

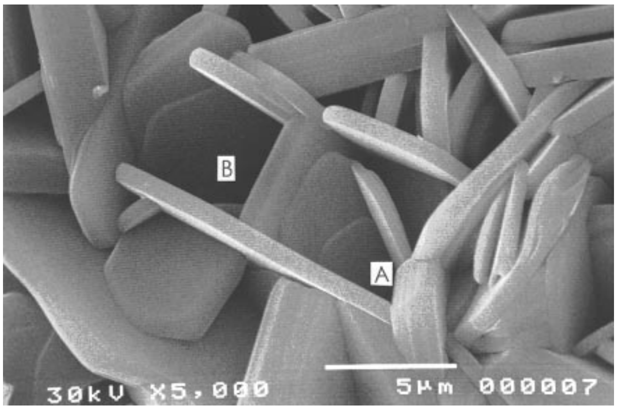

Fig. 2 Scanning electron micrograph of the potassium salt of the antimonic acid, $KSb(PO_4)_2$, showing the 'deck of cards' type randomly orientated lamellae (see text for key to A and B)

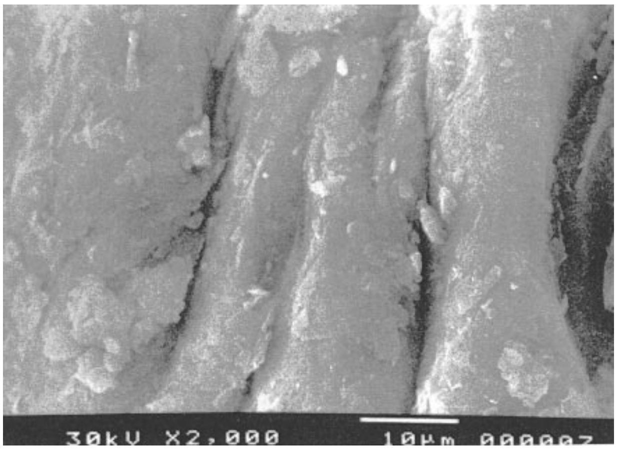

Fig. 3 Scanning electron micrograph of the antimony hydrogen phosphate, $HSb(PO_4)_2{\cdot}2H_2O$, following ion exchange from $KSb(PO_4)_2$. This clearly shows the delamination caused by acid attack.

with little evidence for areas of micro- or meso-porosity between individual crystallites.

X-Ray powder diffraction results

$H_1SbP_2{\cdot}2H_2O$–tetrakis(pyridyl)iron(II) chloride reaction products. Fig. 4(*a*) shows the PXRD pattern obtained for the host $H_1SbP_2{\cdot}2H_2O$ with the indexed values given in Table 1. Previous studies on the host $H_1SbP_2{\cdot}2H_2O$ suggested that the synthesised material had a basal spacing (d_{002}) of *ca.* 10.79 Å.[1] The PXRD pattern observed for the $H_1SbP_2{\cdot}2H_2O$–$[Fe(py)_4Cl_2]$ reaction product is shown in Fig. 4(*b*), with the corresponding observed PXRD data given in Table 2.

The guest complex, which is monoclinic with space group $P2_1/c$, has the following unit-cell dimensions[13] in its 'free' state: $a = 9.384(6)$ Å, $b = 16.766(4)$ Å and $c = 16.342(9)$ Å, $\beta = 121.497(25)°$, $V = 2192.2(1.2)$ Å^3. It is interesting that the main effect of the hydrogen-bonded water molecule is to make each of the four pyridyl groups crystallographically non-equivalent.[13] PXRD studies on the $H_1SbP_2{\cdot}2H_2O$–$[Fe(py)_4Cl_2]$ reaction products showed the average increase in basal spacing of the $H_1SbP_2{\cdot}2H_2O$ after reaction to be only *ca.* 3 Å to a new basal spacing of 12.23 Å. The intercalation mechanism of $H_1SbP_2{\cdot}2H_2O$ is thought to be driven by the loss of the two moles of interlayer water.[1] Therefore, assuming this to be the case (see FTIR results), the actual height of the intercalated complex is *ca.* 5.44 Å in the interlayer. The most likely interpretation of these results is that the water of crystallisation of the complex is intercalated into the interlayer region of the H_1SbP_2. Previous results suggested that the basal spacing of a high-water content H_1SbP_2 is often > 10.4 Å. It was thought to be unlikely that the complex itself lays flat between adjacent H_1SbP_2 lamellae with the removal of both its water of crystallisation and the ($2 \times Cl^-$) charge balancing anions. The polyphasic nature of the PXRD patterns obtained for the reaction products suggested that the composition included some regions of chemically unaltered phosphate groups as well as areas of surface sorbed $[Fe(py)_4]^{2+}$ cationic species. The exact nature of these species can not be deduced from PXRD; however, NMR studies suggested that several associations with the phosphate tetrahedra were possible. These are shown schematically in Fig. 5.

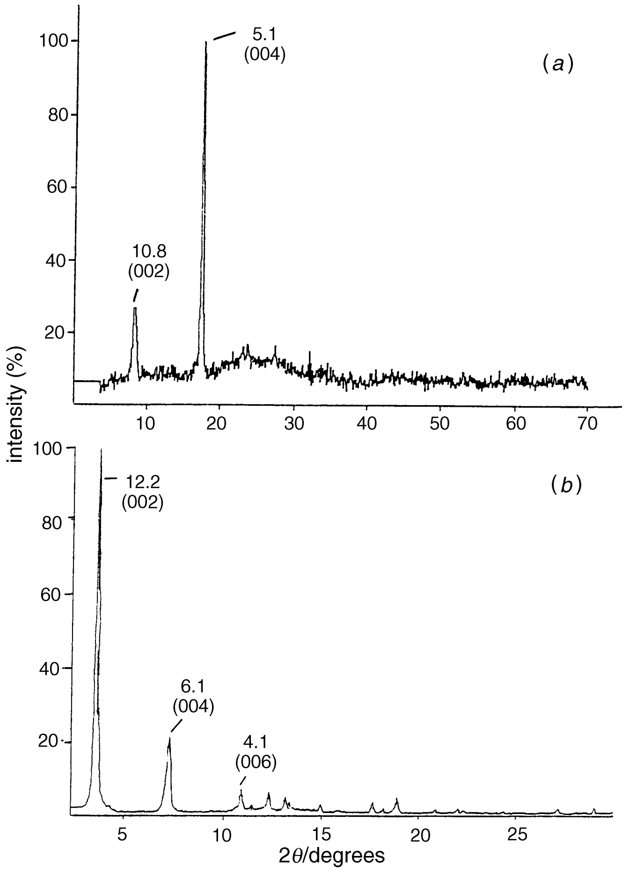

Fig. 4 PXRD patterns for (*a*) $H_1SbP_2{\cdot}2H_2O$ and (*b*) $H_1SbP_2{\cdot}2H_2O$–$[Fe(py)_4Cl_2]$ reaction products

Table 1 Observed powder X-ray diffraction data for $H_1SbP_2{\cdot}2H_2O$ host material[a]

2θ/degrees	*d*/Å	I/I_0 (%)	assigned Miller indices *hkl*
8.19	10.79	24.2	002[b]
8.46	10.44	17.5	002
17.42	5.09	100.0	004
23.04	3.86	2.2	—
23.96	3.71	17.2	—
27.27	3.27	2.5	—

[a] All reflections were indexed to synthetic antimony hydrogen phosphate using JCPDS card no. 39-62 and ref. 1. [b] This reflection was taken as the d_{002} basal spacing reflecting the high water content of the material. The second d_{002} listed reflects a second phase with slightly lower water content.

The possibility of the formation of a kind of 'chain polymer' with Fe—O bridges between the adjacent H_1SbP_2 lamellae (in the form of an intercalate) was thought to be unlikely compared to intercalation of an extra layer(s) of water molecules. No evidence was found for the former hypothesis in any of the techniques used, including FTIR spectroscopy.

Table 2 Observed powder X-ray diffraction data for the $H_1SbP_2\cdot 2H_2O-[Fe(py)_4Cl_2]$ reaction products

2θ/degrees	d/Å	I/I_0 (%)	assigned Miller indices hkl
3.61	12.23	100.00	002[a]
7.30	6.06	21.00	004[a]
10.93	4.06	7.10	006[a]
11.45	3.88	3.40	—
12.31	3.61	6.90	—
13.17	3.38	5.50	—
13.38	3.33	4.00	—
14.95	2.99	3.20	—
17.66	2.54	4.30	—
18.21	2.47	2.00	—
18.91	2.38	5.10	—

[a] Reflections assigned to phase containing $[Fe(py)_4]^{2+}$ cations using synthetic antimony hydrogen phosphate and JCPDS card no. 39–62 and ref. 1. All remaining reflections were assumed to arise from either unreacted $H_1SbP_2\cdot 2H_2O$ or the reaction product but could not be indexed with any degree of certainty.

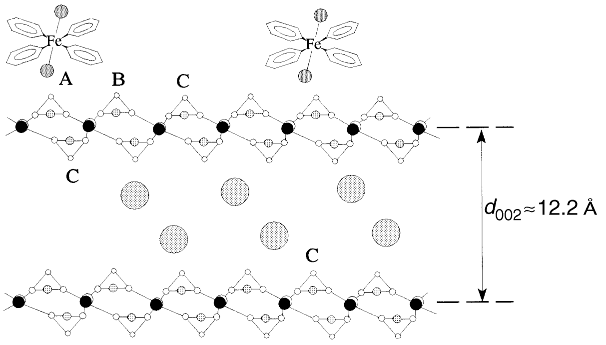

Fig. 5 Schematic diagram showing the proposed structure of the $H_1SbP_2\cdot 2H_2O-[Fe(py)_4Cl_2]$ reaction products

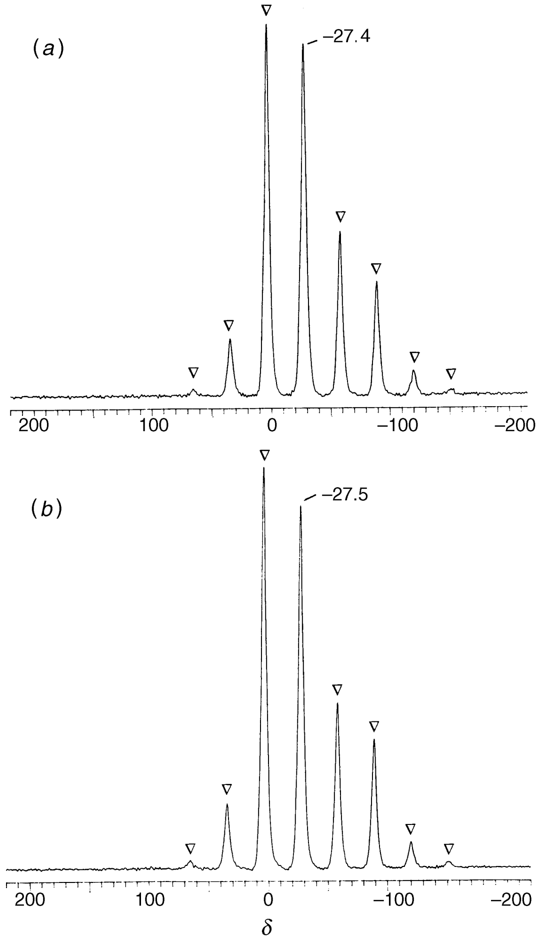

Fig. 6 ^{31}P MAS NMR spectra of $H_1SbP_2\cdot 2H_2O$ obtained using (*a*) single-pulse, (*b*) cross-polarization techniques. Some experimental conditions for (*a*) include gated decoupling; pulse width = 90°; number of repetitions = 4, and for (*b*) include flip-back; contact time = 3 ms, number of repetitions = 500; spectral width = 100 kHz and spin rate = 3760 Hz in both cases. (▽ indicate spinning side bands.)

Solid-state MAS NMR spectroscopy

^{31}P MAS NMR spectra of the host $H_1SbP_2\cdot 2H_2O$. In a previous study on antimonic acids and their precursor salts Taulelle *et al.*[14] showed that the experimentally observed ^{31}P MAS NMR line moves to a higher field position when the number of bridging oxygens in the PO_4 groups increases. It is possible to consider the connectivity of the central phosphorus atom in these PO_4 groups in a similar manner to that already applied, for example, to aluminium atoms in zeolites, using the so-called Q notation.[15,16] Using this notation, the number of bridging oxygens between the central phosphorus and the metal (antimony) centres are given a value between Q^0 (for zero connectivity) and Q^4 (for four connecting Sb—O—P bonds in the phosphate groups). It has been found that the parent $H_1SbP_2\cdot 2H_2O$ has phosphate groups with a connectivity of Q^3; *i.e.* 3(Sb—O—P) bonds with the fourth oxygen being part of the P—OH group.[11]

The ^{31}P MAS single-pulse (SP) and cross-polarised (CP) NMR spectra of $H_1SbP_2\cdot 2H_2O$ are shown in Fig. 6(*a*) and (*b*) respectively. The spectrum run with a single pulse shows a single resonance at −27.4 ppm. Since the relaxation delay used to obtain this spectrum was high (300 s), the relative intensity of the phosphorus resonance in the sample is directly proportional to the amount of the phosphorus group giving rise to that resonance in the material.[17] Clearly, there are no other phosphorus-containing species present in the sample at room temperature.

The cross-polarised spectrum also shows a single phosphorus resonance at −27.5 ppm. In general, we have found that this single (Q^3) phosphate resonance occurs within the range −23 to −28 ppm, which is considerably lower than for other Q^3 groups in phosphates, although the actual chemical shift of this resonance was found to vary with each synthesised batch of $H_1SbP_2\cdot 2H_2O$. The CP experiment relies upon the 'through space' dipolar coupling between ^1H and ^{31}P nuclei. The CP experiment is important because any PO_4 groups present in the sample (and in the SP spectrum) without any associated protons would not be visible in the CP spectrum. Clearly, the fact that the same resonance is present in both the CP and SP spectra suggests that all the PO_4 groups present in the sample have some kind of association with protons. This, in turn, suggests that some of the water of crystallisation is involved in an interaction with the PO_4 groups. The formula of this material may, therefore, be written more accurately as $H(PO_4)Sb(PO_4)H_2O\cdot H_2O$, where the protons and water molecules are in a dynamic equilibrium.

Effects of calcination upon the ^{31}P MAS NMR spectra of the host $H_1SbP_2\cdot 2H_2O$. The ^{31}P MAS NMR single-pulse spectra obtained for samples of $H_1SbP_2\cdot 2H_2O$ heated to (i) 300 °C and (ii) 850 °C (prior to cooling and subsequent NMR experiments) are shown in Fig. 7(*b*) and (*c*) with the sample run at ambient temperature being included for comparison [Fig. 7(*a*)]. The spectrum of the sample heated to 300 °C [Fig. 7(*b*)] shows a single resonance at −22.9 ppm. This may be compared to a value of −23.9 ppm observed for the parent (uncalcined) $H_1SbP_2\cdot 2H_2O$ sample used in the heating experiments. This suggests that calcination to 300 °C has little effect upon the overall populations of the types of phosphorus atoms in the PO_4 groups. This is probably caused by the capacity of

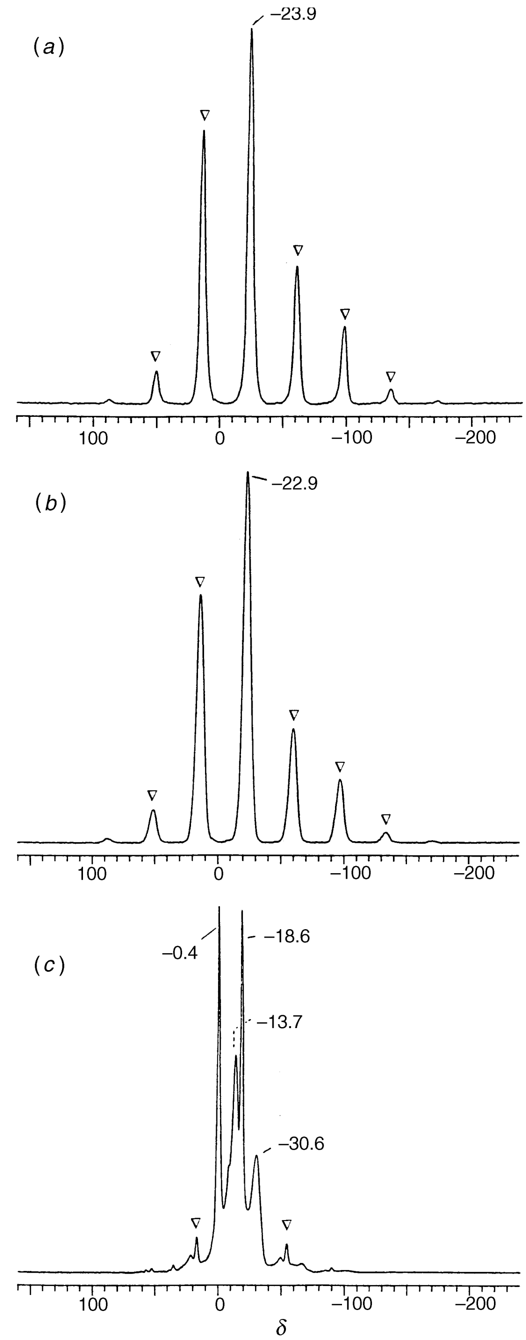

Fig. 7 ^{31}P single-pulse MAS NMR spectra of $H_1SbP_2{\cdot}2H_2O$ at (*a*) ambient temperature, (*b*) heated to 300 °C (prior to NMR) and (*c*) heated to 850 °C (prior to NMR). Experimental conditions include: gated decoupling; pulse width = 90°; number of repetitions = 16, 16 and 300. spectral width = 100 kHz in each case; spin rate = 4520, 4500 and 4400 Hz respectively. (▽ indicate spinning side bands.)

the material to readily readsorb interlayer water and, hence, the protons previously removed. This is consistent with results in which the material was found to (visibly) take up water from the laboratory atmosphere.[6]

The sample heated to 850 °C prior to NMR analysis showed several changes in the phosphorus populations as expected. The resonance at −30.6 ppm was indicative of unaltered PO_4 units thought to be caused by the readsorption of atmospheric water prior to the NMR experiment. The resonances at −18.6, −13.7 and −0.4 ppm were all indicative of new phosphorus species formed by the calcination process. Results obtained for the intercalation of amines into $H_1SbP_2{\cdot}2H_2O$ suggested that the resonance at −18.6 ppm was caused by a PO_4 group without an associated proton.[18] This was to be expected as the calcination temperature of 850 °C would, almost certainly, lead to the formation of the pyrophosphate *via* dehydroxylation of the PO_4 groups after the loss of the interlayer water. The resonances at −13.7 and −0.4 ppm are thought to arise from the pyrophosphate structure consisting of cross-linked $(O_3)\!-\!P\!-\!O\!-\!P\!-\!(O_3)$ groups. The surface of the pyrophosphate is made up of $(O_3)\!-\!P\!-\!O^+$ groups which have totally dissociated from their protons. Although it is difficult to equate crystallinity to the 'sharpness' of NMR lines[19] the overall sharpness of the observed spectrum is suggestive of a well ordered surface.

^{1}H MAS NMR spectrum of $H_1SbP_2{\cdot}2H_2O$. The proton MAS NMR spectrum of $H_1SbP_2{\cdot}2H_2O$ is shown in Fig. 8(*a*). This shows two resonances at +9 and +1.2 ppm. The broad nature of the +9 ppm resonance suggests that there are other resonance which are hidden underneath this lineshape. The presence of the spinning side bands (ssbs) at +40 and *ca.* −21 ppm may possibly indicate the presence of the so-called 'Pake doublet' at room temperature,[20] although this is not as clear as that exhibited in other studies on similar layered materials.[21] For a rigid lattice Pake and Gutowski suggested a splitting of *ca.* 46 kHz was expected.[20] It may or may not be the case that the all first-order ssbs in the observed proton NMR spectra are, in fact, representative of Pake doublets. If the assumption of Pake holds in the present case, the calculated splitting of 18.29 kHz suggests that the $H_1SbP_2{\cdot}2H_2O$ lattice is not rigid at ambient temperature.

Effects of calcination upon the ^{1}H MAS NMR spectrum of $H_1SbP_2{\cdot}2H_2O$. The NMR spectra of $H_1SbP_2{\cdot}2H_2O$ calcined to 300 and 850 °C are shown in Fig. 8(*b*) and (*c*) respectively. The sample heated to 300 °C shows an increased number of observed resonances. It may be surmised that these were present in the original room-temperature spectrum of the $H_1SbP_2{\cdot}2H_2O$. The multiplicity of proton resonances at this temperature may be explained by the fact that the sample loses interlayer water at 300 °C (ref. 6) and this may simply relate to highly mobile interlayer water within the two-dimensional lattice of the $H_1SbP_2{\cdot}2H_2O$. Further heating to 850 °C resulted in the loss of all interlayer water species. The single sharp resonance at +10.3 ppm was thought to represent the $PO_4^-(H^+)$ protonated phosphate groups in the interlayer and exterior surfaces of the H_1SbP_2 crystallites. Again, the use of calculated Pake splittings of 18.59 and 18.24 kHz suggested that the H_1SbP_2 lattice was not rigid, and that calcination had little effect upon the eventual rigidity of the lattice once it cooled down to ambient temperature prior to the NMR experiment. The similarity of all three calculated Pake splittings suggests that they arise from the same protonic species and, therefore, may readily illustrate the ability of the H_1SbP_2 to reabsorb atmospheric water.

^{31}P MAS NMR spectra of the H_1SbP_2–tetrakis(pyridyl)iron(II) chloride reaction products. The ^{31}P MAS NMR spectrum of the host $H_1SbP_2{\cdot}2H_2O$ has been considered elsewhere.[1] The ^{31}P MAS single-pulse (SP) and cross-polarised (CP) NMR spectra of the H_1SbP_2–$[Fe(py)_4Cl_2]$ reaction products are shown in Fig. 9(*a*) and (*b*) respectively. The sample run with a single-pulse showed a total of three resonances at −18.5, −23.9 and −26.7 ppm together with two well defined orders of spinning side bands (ssbs; marked on the spectra as ∇). The high relaxation delay (300 s) used to obtain this spectrum meant that the relative intensity of the phosphorus resonances in the spectrum was directly proportional to the relative proportions of the three types of phosphorus groups giving rise to the resonances in the solid sample.[17]

The cross-polarised spectrum only shows two phosphorus resonances at −24.3 and −26.7 ppm. This spectrum also exhibited two well defined orders of ssbs. We have found[1,6,11]

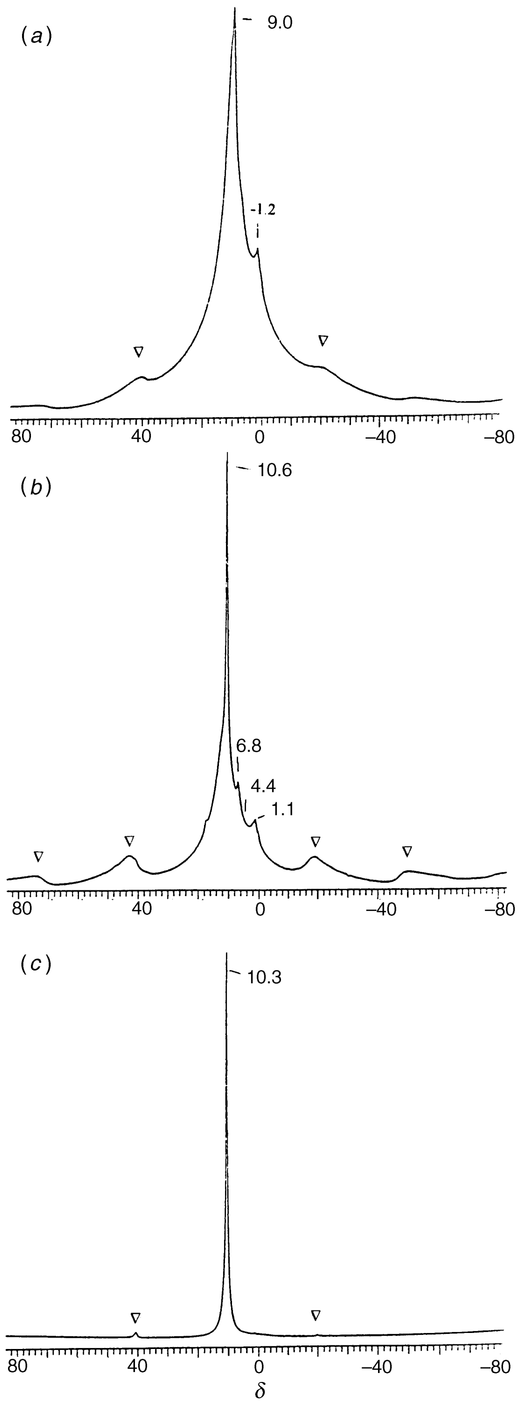

Fig. 8 ^1H MAS NMR spectra of $H_1SbP_2 \cdot 2H_2O$ at (*a*) ambient temperature, (*b*) heated to 300 °C (prior to NMR) and (*c*) heated to 850 °C (prior to NMR). Experimental conditions include: pulse width = 90°; number of repetitions = 200, 200 and 500 respectively. spectral width = 50 000 Hz in each case; spin rate = 8900, 8980 and 9000 Hz respectively. (▽ indicate spinning side bands.)

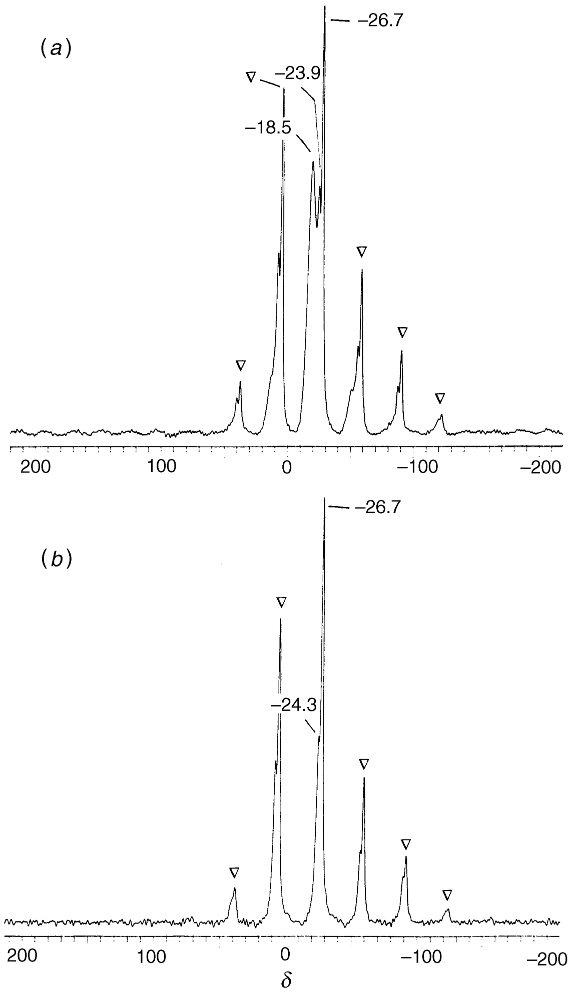

Fig. 9 ^{31}P MAS NMR spectra NMR of $H_1SbP_2 \cdot 2H_2O$–$[Fe(py)_4Cl_2]$ reaction products using (*a*) single-pulse and (*b*) cross-polarisation techniques. Some experimental conditions for (*a*) include gated decoupling; pulse width = 90°; number of repetitions = 4, and for (*b*) include flip-back; contact time = 3 ms; number of repetitions = 500; spectral width = 100 kHz and spin rate = 3800 and 3830 Hz respectively. (▽ denote spinning side bands.)

that for the unreacted host $H_1SbP_2 \cdot 2H_2O$ the resonance which corresponds to $-PO_4$ groups with an associated proton from either the free H^+ and/or H_2O of crystallisation occurs within the range −23 to −28 ppm with the observed chemical shift of this resonance varying with each synthesised batch of antimonic acid. On average, the chemical shifts of the phosphate groups in the host $H_1SbP_2 \cdot 2H_2O$ were found to be approximately −27 ppm and are marked C in Fig. 5. The CP experiment relies upon the through space dipolar coupling between the protons and the ^{31}P nuclei. Clearly, the fact that the −18.5 ppm resonance found in the SP spectrum is not present in the CP spectrum is suggestive of a phosphorus group without an associated proton present in the reaction products; *i.e.* directly bonded to the $[Fe(py)_4]^{2+}$ guest cation to give an octahedral structure which we denote as $Q_B{}^3$, marked A in Fig. 5.

Previous studies attempting to intercalate ferroin, $[Fe(phen)_3]^{3+}$, into H_1SbP_2 have yielded similar MAS NMR results[6] with the SP spectra giving resonances at −18.2 and −27.3 ppm and the corresponding CP spectra showing a resonance at −27.4 ppm. As it is known (from PXRD results) that ferroin does not intercalate into the interlayer of the H_1SbP_2 (owing to the large size of the cation) the −18.2 ppm resonance was thought to arise from a phosphate group (minus its proton) on the exterior crystallite surface bonded directly to the ferroin complex.

The remaining phosphate group SP spectrum of the H_1SbP_2–$[Fe(py)_4Cl_2]$ reaction products was not thought to differ much from the unchanged phosphate group at −26.7 ppm (Q^3). The difference in chemical shift was thought to have been caused by the perturbation of the protonated phosphate group by the sorbed $[Fe(py)_4]^{2+}$ and was, therefore, denoted as $Q_P{}^3$, marked B in Fig. 5.

Deconvolution of the three resonances in the SP spectrum of the reaction products in the present study (taking into account the first order of spinning side bands) suggested that the relative populations of the three phosphorus species were: −18.5 ppm, 56%; −23.9 ppm, 18%; and −26.7 ppm, 26%.

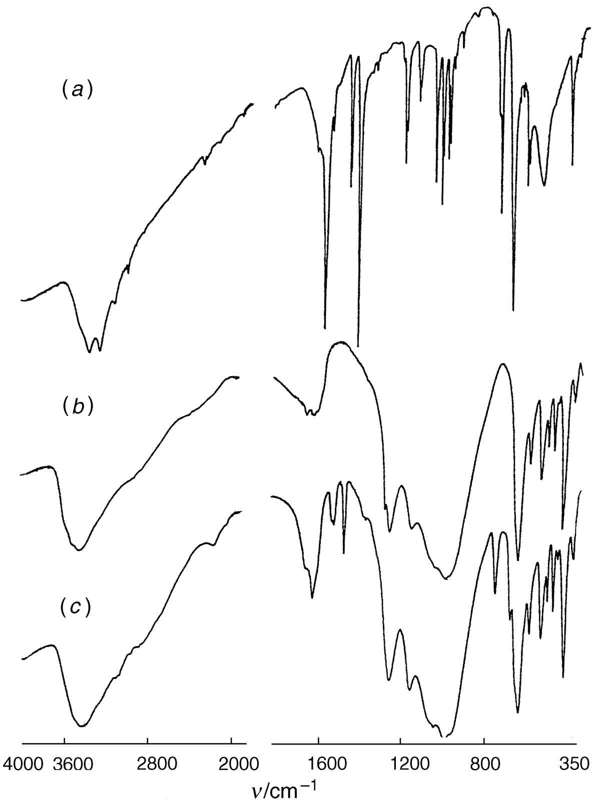

Fig. 10 FTIR spectra of (*a*) $Fe(py)_4Cl_2{\cdot}H_2O$, (*b*) $H_1SbP_2{\cdot}2H_2O$ and (*c*) the $H_1SbP_2{\cdot}2H_2O$–$[Fe(py)_4Cl_2]$ reaction product

This, in turn, suggested that the total number of sorbed phosphorus groups in the material was over 50% of the original surface phosphate groups of the antimonic acid host.

FTIR studies

FTIR studies on the host $H_1SbP_2{\cdot}2H_2O$ have been detailed elsewhere.[1,3,22,23] Fig. 10(*b*) shows the FTIR spectrum observed for $H_1Sb(PO_4)_2{\cdot}2H_2O$ while Fig. 10(*a*) shows the FTIR spectrum obtained for $[Fe(py)_4Cl_2]{\cdot}2H_2O$. The FTIR spectrum observed for the reaction product [Fig. 10(*c*)] clearly approximates to the summation of the two previous spectra. This is to be expected as it has been found that this behaviour is common in antimony hydrogen phosphate intercalation compounds.[22] All of the three spectra show characteristic peaks for water. The $H_1SbP_2{\cdot}2H_2O$ [Fig. 10(*b*)] and the reaction products [Fig. 10(*c*)] both show a broad hydrogen-bonded —OH group stretch.[22,23] The presence of water in the reaction products was thought to arise from the material's ability to readsorb atmospheric water as well as the aqueous ligands of the complex. This water was thought to be possibly present in the interlayer region, as well as on the outer surface of the crystallites. $[Fe(py)_4Cl_2]{\cdot}2H_2O$ [Fig. 10(*a*)] shows this stretch as well as a peak at 3319 cm^{-1} which is thought to arise from water of crystallisation of the complex.

The reaction product [Fig. 10(*c*)] show several resonances which arise from the pyridine ring structures in the complex. These occur in the region 2250 to 1488 cm^{-1}, 752 and 680 cm^{-1}. In particular the band at 752 cm^{-1} is characteristic of four adjacent C—H groups on an aromatic ring. The bands at 636, 586, 500 and 472 cm^{-1} correspond exactly to those in the spectrum of $H_1SbP_2{\cdot}2H_2O$. These bands (below 700 cm^{-1}) may be assigned as Sb—O stretching modes, whilst those above 1000 cm^{-1} mostly conform to P=O, P—O—P or P—O terminal group stretching modes from the $H_1SbP_2{\cdot}2H_2O$ lattice structure. To any degree of certainty no bands characteristic of Fe—O bonds were observed in the FTIR spectrum.

Conclusions

Scanning electron microscopy (SEM) conclusively showed that the crystalline K_1SbP_2 consisted of the so-called 'deck of cards' arrangement of randomly orientated lamellae. SEM also indicated that the attack of acid (used in the synthesis of the title compound) resulted in the effective delamination of these lamellae. Intercalation studies carried out using tetrakis(pyridyl)iron(II) chloride suggested that the $[Fe(py)_4]^{2+}{\cdot}H_2O$ species was not intercalated as a flattened (dissociated) complex {*i.e.* as the $[Fe(py)_4]^{2+}$ complex} between adjacent layers of the $H_1SbP_2{\cdot}2H_2O$ as was first thought, but rather, was surface sorbed. ^{31}P MAS NMR studies indicated that the $H_1SbP_2{\cdot}2H_2O$–$[Fe(py)_4]$ reaction products contained phosphate group resonances which could be readily assigned as belonging to (i) chemically unaltered host $H_1SbP_2{\cdot}2H_2O$ (protonated Q^3) phosphate groups, (ii) phosphate groups bonded to the cationic species (denoted $Q_B{}^3$). In addition to these, a separate resonance was also noted which was thought to arise from a chemically unaltered phosphate group of the host $H_1SbP_2{\cdot}2H_2O$, but which was perturbed by the close proximity of the aromatic charge in the $[Fe(py)_4]^{2+}$ cationic species. This new resonance was denoted as $Q_P{}^3$. Phosphorus NMR studies on ferroin intercalation into $H_1SbP_2{\cdot}2H_2O$ confirmed that the $[Fe(py)_4]^{2+}$ complex was surface sorbed.

The authors should like to thank Laporte Research and Development for financial support for S. C. and A. E. A. Technology (Harwell) Ltd. for financial support for W. L. We are also grateful to Professor R. Harris and Dr D. C. Apperley of the EPSRC Solid-state NMR Service, Industrial Research Laboratories, University of Durham, for the NMR spectra.

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Paper 7/00151G; *Received* 7*th January*, 1997