Journal of Inclusion Phenomena and Molecular Recognition in Chemistry 7: 301–308, 1989.

Intercalation of Monomers into Alpha Tin(IV) Hydrogen Phosphate

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(Received: 11 February 1988; in final form: 11 July 1988)

Abstract. Monomers which contain unsaturated linkages and amine groups have been intercalated to form either mono- or bi-layers. The monomer *trans-N,N′*-diethyl-2-butene-1,4-diamine (NNBD) has been intercalated into α-tin(IV) hydrogen phosphate. The guest molecule, NNBD, forms a monolayer ($d_{001} = 1.35$ nm) in which the amine groups are paired to protons on opposite faces of the phosphate layers. The resultant compound has the formula $Sn(C_8H_{18}N_2)_{0.73}(HPO_4)_2 \cdot H_2O$ indicating that NNBD does not cover a large proportion of the available protons. 4-vinylpyridine slowly forms an intercalate in which the host molecule forms a bilayer ($d_{001} = 1.56$ nm). However, with 4-vinylpyridine there is surface modification in preference to intercalation.

Key words. α-Tin(IV) hydrogen phosphate, intercalation, surface modification, monomers, trans-*N,N′*-diethyl-2-butene-1,4-diamine, 4-vinylpyridine, tetraethylenepentamine.

1. Introduction

The principal interests in intercalation stem from the need to develop new materials with improved mechanical or electrical properties. Such materials could find application in biosensors, solid state batteries and composite materials. Little work has been reported regarding the intercalation of unsaturated monomers and consequently the conditions under which surface modification or intercalation occurs have not been established. Amino acids, which may be considered to be monomers, have been intercalated [1, 2] in α-phosphates. Within the context of this paper, surface modification means the acid–base interactions between the surface POH groups and Brönsted bases. Such interactions always take place when a protonatable species is intercalated. In usual preparations of layered phosphates the surface area ranges between 1–10 $m^2 g^{-1}$ and the concentration of the surface POH groups is between 0.1 and 1% of the total. The presence of Lewis acid sites (electron-pair accepting) may be normally excluded with respect to bulk and surface groups except when there are hydrolysed tin(IV) atoms which are not bound to phosphates. Moreover, there have been few studies on the intercalation compounds of α-tin(IV) hydrogen phosphate monohydrate $Sn(HPO_4)_2 \cdot H_2O$. The Group IVB phosphates

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form layer compounds of two types: those with a relatively small interlayer spacing (0.79 nm), the so-called α-type, and those with a larger interlayer spacing [3] (1.2 nm) of the γ-type. The α-form of tin(IV) hydrogen phosphate was used here. This has a structure which is similar to that of crystalline α-zirconium hydrogen phosphate [4] and has an interlayer spacing, $d_{002} = 0.79$ nm, in the unmodified material. It has been reported previously [5–7] that amines may be intercalated by α-tin(IV) hydrogen phosphate. Pyridine gives an intercalation compound in which there is a small increase in the *d*-spacing of 0.45 nm. The reason for the small increase is that the pyridine molecules lie nearly parallel to the phosphate layers. The resulting compound $Sn(C_5H_5N)_{0.4}(HPO_4)_2 \cdot H_2O$ only has a small proportion of pyridine because the molecule covers the otherwise available protons. Piperidine ($d_{001} = 1.57$ nm), aniline and *m*-toluidine all form bilayers. There were indications that the surface groups such as pyridine (i.e. those that are bound to the α-tin(IV) hydrogen phosphate but are not intercalated) may be partially removed by equilibration in the vapour over concentrated sulphuric acid.

2. Experimental

The α-tin(IV) hydrogen phosphate $Sn(HPO_4)_2 \cdot H_2O$ was prepared and analysed as described previously [5]. The partially exchanged copper material was prepared by equilibrating the α-$Sn(HPO_4)_2 \cdot H_2O$ in an excess of 0.01M copper(II) nitrate solution for ten minutes. The NNBD intercalates were prepared by either equilibrating 0.5 g of α-$Sn(HPO_4)_2 \cdot H_2O$ with NNBD (0.22 g) in toluene (25 cm^3) or in water at 30°C for two days. The suspension was filtered, washed with acetone and air dried. The remaining intercalates were obtained by equilibrating the α-$Sn(HPO_4)_2 \cdot H_2O$ or the partially exchanged copper compounds with the vapour or an aqueous solution for seven hours. The intercalation compound with 4-vinylpyridine did not form from a toluene solution. The intercalation compound was formed by immersing the α-tin(IV) hydrogen phosphate in undiluted 4-vinylpyridine for seven days. The tetramethylenepentamine (PAM) intercalates were prepared by equilibration of α-$Sn(HPO_4)_2 \cdot H_2O$ with an aqueous solution containing one mole equivalent of PAM. The phosphate dissolved completely when more PAM was present. **Warning:** as indicated in the text, this compound 'goes off like a firework' when being studied by thermal analysis and this should therefore be avoided.

The NNBD-α-$Sn(HPO_4)_2 \cdot H_2O$ complex was analysed by CHN analysis and by thermal analysis. The formula found from the thermal analysis results was $Sn(C_8H_{18}N_2)_{0.73} \cdot (HPO_4)_2 \cdot H_2O$. That found by CHN analysis are as follows (values calculated for the above formulation are in parenthesis) C: 16.58(16.2); H: 4.13(3.96); N: 4.63(4.73).

The ESR spectra were recorded on a Varian E-3 spectrometer. The thermal analytical data were recorded on a Rigaku thermoflex and the X-ray powder diffraction patterns were recorded on a Siemens D-500 diffractometer with a graphite monochromator. Surface area measurements were taken using the BET method.

3. Results and Discussion

A preliminary communication [8] concerning part of this work has been published previously. Some interlayer distances [9] of products from the reaction with amines and tin(IV) hydrogen phosphate or its partially exchanged copper or nickel derivative are shown in Table I. The weak base pyridine seems to be at the borderline concerning intercalation or surface modification as in some samples there was no intercalation but with others, such as when α-tin(IV) hydrogen phosphate was equilibrated with pyridine vapour, there was intercalation to give a compound of formula $Sn(C_5H_5N)_{0.4}(HPO_4)_2{\cdot}H_2O$. The stronger bases ethylenediamine and PAM $\{NH(CH_2CH_2NH{\cdot}CH_2CH_2NH_2)_2\}$ were readily intercalated with the large expansion of 1.1 nm resulting from the PAM intercalation compound. This 1.1 expansion implies that at least part of the PAM molecule is acting as a bridge between the phosphate layers and occurred whether the PAM was in aqueous solution or present as vapour. Thermal analysis of the PAM intercalation compound was not possible because the compound **decomposed violently on heating**. When ethylenediamine or PAM formed intercalation compounds with either α-$Sn(HPO_4)_2{\cdot}H_2O$ or its partially exchanged copper derivative, the *d*-spacings were the same and the copper electron spin resonance spectra do not resemble [10] the known spectra of copper amine compounds but were characteristic of copper(II) aquo complexes. It appears, therefore, that the amines are principally bound to protons rather than coordinated to copper. Consequently, in subsequent experiments with monomers only the tin(IV) hydrogen phosphate was used and not the partially exchanged metal derivatives. In the α-phosphates there are arguably two types [11] of acid sites – one strong proton donating site and the other one which is capable of accepting electron pairs. The bases such as PAM probably saturate the strong acid sites as far as possible – both sites are Brönsted (proton exchanging) sites.

Table I. Interlayer distances of products from the reaction with amines and tin(IV) hydrogen phosphate or its metal-partially exchanged derivatives[a]

Entry		Reactants	Interlayer distance/nm
1	Phosphate A	–	0.796
2	Phosphate A(Cu)	NH_3(aq.)	0.89
3	Phosphate A(Cu)	Pyridine(aq.)	0.81 (broadened)
4	Phosphate A	Pyridine (V)	1.15 (one sample)
5	Phosphate A(Cu,Ni)	$H_2NCH_2CH_2NH_2$(aq.)	1.09
6	Phosphate A(Cu)	PAM (aq. V)	1.89
7	Phosphate A	*trans*-NNBD(V)	1.38
8[b]	Phosphate A	*trans*-NNBD(tol)	1.35
9[b]	Phosphate A	8 heated to 60°C	1.33
10[b]	Phosphate A	8 heated to 120°C	1.206

[a] A(Cu) = copper exchanged tin(IV) phosphate; PAM = $NH(CH_2CH_2NHCH_2CH_2NH_2)_2$; *trans*-NNBD = *trans*-$EtNHCH_2CH{=}CHCH_2NHEt$; aq. = aqueous; V = vapour phase. The partially exchanged materials were prepared by reaction of the tin(IV) phosphate with 0.01M metal nitrate solution (10 min, ambient temp.).

[b] 1 : 1 molar ratio; tol = toluene.

The aim of this work was to intercalate monomers with unsaturated linkages into α-tin(IV) hydrogen phosphate. It appeared possible to speculate on the basis of the data in Table I that monomers with aliphatic or strong base amine groups could form intercalation compounds by an acid–base reaction with proton donating sites. Those with weaker base groups might only modify the surface groups. Since α-$Sn(HPO_4)_2 \cdot H_2O$ is hydrophilic, the presence of hydrophobic groups such as the vinyl groups could further reduce the ability of the monomer to intercalate. However, the presence of hydrophobic groups may facilitate the aggregation of the guests in the layer region. These effects were studied with 4-vinylpyridine.

3.1. BILAYERS OF 4-VINYLPYRIDINE

When 4-vinylpyridine was dissolved in toluene and the solution equilibrated with the phosphate, there was no intercalation. After equilibration in liquid 4-vinylpyridine for seven days there was a weak reflection (see Table II) at 1.56 nm corresponding to an increased *d*-spacing (002) of approximately 0.74 nm. This value is comparable to that (0.74 nm) obtained when bilayers of piperidine are formed in the host. It appears likely, therefore, that the 4-vinylpyridine is intercalated to a small extent as a bilayer. Probably the amine groups are bound to proton sites on opposite phosphate layers with the vinyl groups close to one another (see Figure 1). There was no evidence of a monolayer and perhaps the 4-vinylpyridine units diffused in as a bilayer. However, the intercalation experiments were performed in such a way as to yield equilibrium results. It is possible, of course, that a monolayer would be an intermediate. The compound analysed as $Sn(C_7H_7N)_{0.76}(HPO_4)_2 \cdot H_2O$ prior to equilibration with concentrated sulphuric acid vapour. Since the 002 reflection at 1.57 nm is weak, the high value of 0.76 moles of 4-vinylpyridine indicates that there is a considerable amount of surface modification in preference to intercalation into the host structure. The thermal analysis data were similar to

Table II. X-ray powder diffraction data for pyridine with α-tin(IV) hydrogen phosphate and 4-vinylpyridine with α-tin(IV) hydrogen phosphate; $\lambda = 0.15418$ nm

Pyridine with α-$Sn(HPO_4)_2 \cdot H_2O$		4-vinylpyridine with α-$Sn(HPO_2)_2 \cdot H_2O$*	
Assignment (*hkl*)	d_{hkl}/nm	Assignment (*hkl*)	d_{hkl}/nm
002	1.148	002	1.564
004	1.574	004	0.788
110	0.423	110	0.422
200	0.404		
006	0.382		
202	0.342	111	0.346
020	0.248	020	0.248
220	0.211	310	0.237
400	0.202		0.215
130	0.163	130	0.162
330	0.144		0.157

* $Sn(C_7H_7N)_{0.76}(HPO_4)_2 \cdot H_2O$ (including surface coverage) but after washing with acetone.

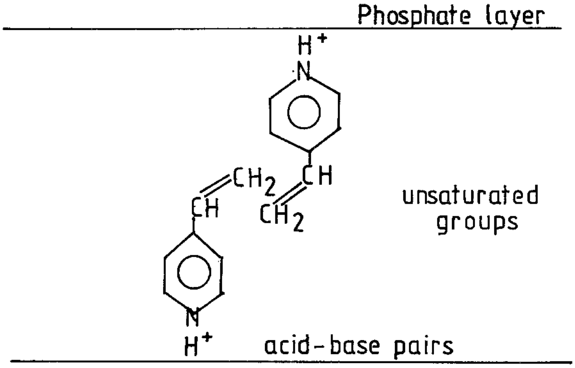

Fig. 1. Bilayer of 4-vinylpyridine in α-tin(IV) hydrogen phosphate monohydrate, α-$Sn(HPO_4)_2 \cdot H_2O$.

those with NNBD but with an additional sharp peak at 310°C. The surface area of α tin hydrogen phosphate was determined to be between 1–10 $m^2 g^{-1}$. If there was a simple surface modification, the extent of adsorption would be expected to be in the range of 1–10 μmole g^{-1}. Since the value is much higher than this there would have been some delamination or exfoliation leading to an increase in surface area. This effect is being studied further.

3.2. MONOLAYERS OF *TRANS-N,N′*-DIETHYL-2-BUTENE-1,4-DIAMINE

The 4-vinyl group in 4-vinylpyridine is well removed from the weak base heterocyclic nitrogen and it was considered that it might be beneficial to have the vinyl group between two more strongly basic groups. Such a configuration is more likely to act as an intercalated guest molecule than 4-vinylpyridine. With *trans-N,N′*-diethyl-2-butene-1,4-diamine, *trans*-$EtNHCH_2CH{=}CHCH_2NHEt$ (NNBD), the unsaturated group is between two aliphatic nitrogen atoms. (See Figure 2).

The reaction between NNBD in toluene solution with one mole ratio of the insoluble α-$Sn(HPO_4)_2 \cdot H_2O$ gave a compound which analysed as $Sn(C_8H_{18}N_2)_{0.73}(HPO_4)_2 \cdot H_2O$ after equilibration with concentrated sulphuric acid vapour. The X-ray diffraction data for this material are shown as sample A in Table III. Clearly the monomer has been intercalated. In sample A, which had not been

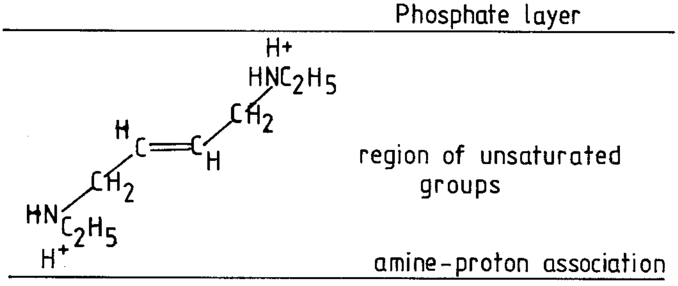

Fig. 2. Monolayer of NNBD in α-$Sn(HPO_4)_2 \cdot H_2O$.

Table III. X-ray powder difraction data for $Sn(NNBD)_{0.73}(HPO_4)_2{\cdot}H_2O$ at different temperatures; $\lambda = 0.15418$ nm

A (30°C)	B(60°C)	C(120°C)	Assignment (*hkl*)
1.35 (100)*	1.33 (100)	1.206 (100)	002
0.776 (18)	0.777 (15)	0.759 (43)	002**
0.675 (18)	0.667 (18)		004
0.425 (35)	0.425 (33)	0.425 (68)	110
0.401 (34)	0.398 (35)		200
0.348 (55)	0.347 (54)		202
0.249 (29)	0.249 (29)	0.249 (42)	020
0.214 (12)	0.210 (12)		220
0.157 (12)	0.157 (12)		130

A, B and C heated to the temperature indicated and cooled.

* (I_0/I);

** Section with no intercalation.

heated above 30°C before measuring the X-ray diffraction data, the expansion over the modified form is 0.52 nm. The reflection at 1.35 nm is clear with an intensity of 100 on the scale on which the 0.776 nm reflection is 18: these relative intensities imply there is extensive intercalation.

The *trans*-isomer was selected because it was considered that it was more likely to bridge the phosphate layers than the *cis*-isomer. Some information can be derived from the value of 0.73 for the NNBD in this formula. With the pyridine intercalate, in which the guest molecules lie parallel to the inorganic layers, the corresponding value is 0.4. This low value was considered to arise because the pyridine molecules have a good covering effect and only 20% of the available H atoms are available for acid–base pairing. With 4,4′-bipyridine the value is 0.25 as this molecule also covers available protons. With *trans*-NNBD, however, the higher value of 0.73 indicates that there is a poor covering effect presumably because the amine groups are paired to opposite faces. If this is the case, the estimated angle of the guest NNBD molecule to the plane is approximately 60°. One possible idealised structure is given in Figure 2. The principal features are the acid–base pairing on opposite faces and the layer of unsaturated molecules in the middle region between the planes. Samples B and C in Table III were heated to 60° and 120°C, respectively, and cooled to ambient temperatures for measurement of the X-ray powder diffraction data. The integrity of the NNBD intercalate was retained at 60°C and the 002 and 004 reflections remain clear. However, when heated to 120°C, below which temperature the loosely bound water molecules are lost, there appears to be a structural change as certain reflections such as the (004) and (002) are missing. The (002) reflection, as expected, has shifted corresponding to a decrease of 0.127 nm which is connected with the loss of water. The essential layer structure is, however, retained because the *nk*0 lines where $h + k \neq 2n$ are absent.

The thermal analysis data are illustrated for sample A (in air) in Figure 3. The peak at 57°C corresponds to an endothermic loss of loosely bound water; 147°C to endothermic loss of bound water; 352°C to exothermic oxidation of NNBD; 500°C to endothermic conversion of phosphate to pyrophosphate; 739°C to an exothermic

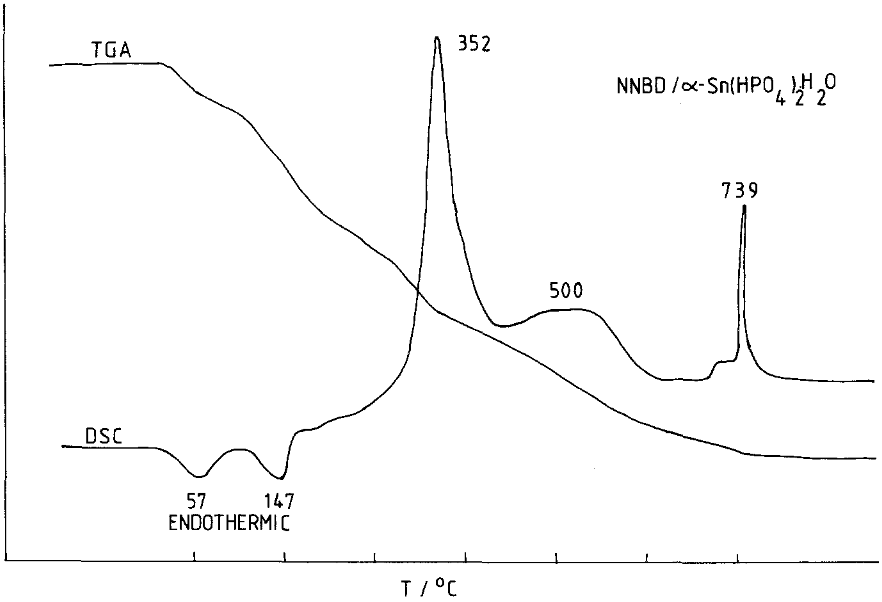

Fig. 3. Thermal analysis of NNBD-α-$Sn(HPO_4)_2 \cdot H_2O$.

oxidation of carbon to volatile oxides (the sample changed from black-grey to white) – this last peak was not seen on every sample.

4. Conclusion

A clear, well defined monolayer of NNBD was formed in a host of α-tin hydrogen phosphate. A less well defined bilayer of 4-vinylpyridine was also formed. Further studies are in progress to extend the range of monomers which can be intercalated.

Acknowledgements

We gratefully acknowledge the support of the British Council and Ministerio de Educaión y Ciencia for travel grants for this project and to Mrs. G.M. Boffey for typing and secretarial help.

References

1. T. Kijima, S. Ueno, and M. Goto: *J. Chem. Soc., Dalton Trans.* 2499 (1982).
2. U. Costantino, M. A. Massucci, A. La Ginestra, A. M. Tarola, and L. Zampa: *J. Incl. Phenom.* **4**, 147 (1986).
3. A. Clearfield, G. H. Nancollas, and R. H. Blessing: in *Ion-Exchange and Solvent Extraction*, eds. J. A. Marinsky and Y. Marcus, Marcel Deker, New York (1973), Vol 5, Chapter 1.
4. A. Clearfield and G. D. Smith: *Inorg. Chem.* **8**, 431 (1969).
5. E. Rodríguez-Castellón, A. Rodriguez Garcia and S. Bruque: *Inorg. Chem.* **24**, 1187 (1985).

6. E. Rodríguez-Castellón, S. Bruque, and A. Rodríguez-Garcia: *J. Chem. Soc., Dalton Trans.* 213 (1985).
7. R. Pozas Tormo, L. Moreno Real, M. Martinez Lara, and E. Rodríguez-Castellón: *Can. J. Chem.* **64**, 35 (1986).
8. I. Fotheringham, C. O. Giwa, and M. J. Hudson: *J. Chem. Soc. Chem. Commun.* 1554 (1986).
9. I. Fotheringham, M.Sc. Thesis, Reading, 1986.
10. A. W. Addison and H. Yokoi: *Inorg. Chem.* **16**, 1241 (1977).
11. S. Yamanaka, Y. Haribe, and M. Tanaka: *J. Inorg. Nucl. Chem.* **38**, 323 (1979).