Compounds of Tin(IV) Phosphate with Monomers: Intercalation or Surface Modification?

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A monomer with *trans* amine groups has been intercalated into tin(IV) phosphate and some criteria for surface modification or intercalation have been established.

There is much current interest in the surface modification of inorganic materials with monomers because the resulting materials may be useful in biosensors, solid state batteries, and composites. Little work, however, has been done with respect to the intercalation and surface modification of tin(IV) phosphate.[1,2] The formation of an intercalation compound may be established by measurement of the d-spacing and some values from the reactions of copper- and nickel-exchanged tin(IV) phosphate with different amines are shown in Table 1 (samples 1—6). The phosphate itself or the metal-exchanged compounds were shaken at ambient temperatures for seven hours with an aqueous solution or with the vapour of the amine. Those with aliphatic groups formed intercalation compounds. Of particular note is the large expansion (1.09 nm) obtained with the amine $NH(CH_2CH_2NHCH_2CH_2NH_2)_2$ which implies that the terminal primary amine groups are probably bound to the adjacent layers. The heterocyclic base, pyridine, seems to be borderline as the intercalation compound was formed from the vapour phase reaction but not from the aqueous phase. The e.s.r. spectrum[3] of the partially copper-exchanged tin phosphate and 1,2-diaminoethane indicates that the compound is principally bound to oxygen rather

Table 1. Interlayer distances of products from the reaction with amines and tin(IV) 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	Pyridine (V)	1.15 (one sample)
5	Phosphate A(Cu,Ni)	$H_2N\,CH_2CH_2NH_2$ (aq.)	1.09
6	Phosphate A(Cu)	PAM (aq. V)	1.89
7	Phosphate A	*trans*-NNBD (V)	1.38
8	Phosphate A	4-Vinylpyridine (V)	0.81 (broadened)

[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 0.01 M metal nitrate solution (10 min, ambient temp.)

than nitrogen so that the amines are involved in reaction with protons rather than ligand exchange with the copper.

In the synthesis of new composite materials, it has been an aim to insert organic monomers between the layers of inorganic compounds. It appeared to be possible to speculate, on the basis of the above data, that monomers with aliphatic amine groups could form intercalation compounds whilst those with weaker base groups might modify only the surface groups. In addition, the vinyl group would reduce the ability of the monomer to intercalate. Clearly those with strong basic groups would also modify the surface but such groups can be removed with acid vapour[1] leaving only the intercalation compound. The partial or complete exchange of protons with copper was not considered to be beneficial. The samples 7 and 8 in Table 1 are both monomers. The *trans*-isomer of NNBD was used as it was hoped to be able to form a new intercalation compound in which the monomer bridges the two layers. The interlayer distance was 1.38 nm which means there was an increase of 0.584 nm. The absence of the *hk*0 planes for $h + k \neq 2n$ implies that the layer structure has been retained. The monomer is lying at an angle of approximately 30° between the two planes. To the best of our knowledge this is the first example in which a monomer has been inserted between the layers.[4] The approximate ratio of the peak heights d (1.38) : d (0.796) is 6 : 1, which indicates that the majority of the layers were separated by the monomer. Following the procedure of Castellon,[1] the peaks are assigned as 1.38 nm(002); 0.43(110); 0.4(202); 0.349(108); 0.249(020); 0.21(220). For the reaction with 4-vinylpyridine, the positions of the peaks remain unchanged from the original phosphate but the intensity of the peak at 0.796 nm is reduced. Thermal analysis, however, does confirm the presence of the monomer, presumably on the surface. The endotherms at 328, 475 (loss of water), and 776 K (phosphate to pyrophosphate) emanate from the phosphate itself but the exotherm with a maximum at 619 K is due to loss of the vinylpyridine of the vinyl monomer. There was a 9% mass loss for this part of the pyrolysis.

The insertion of the monomer (NNBD) between the layers of the tin(IV) phosphate implies that it will be possible to insert a range of monomers with basic groups.

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