Bilayer Formation of 1,4-Diazabicyclo[2.2.2]octane (DABCO); Intercalation in α-Tin Hydrogen Phosphate

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The bisamine 1,4-diazabicyclo[2.2.2]octane (DABCO) has been intercalated into tin(IV) phosphate to give a bilayer and some criteria for bilayer formation with bisamines have been established.

Expanded layer materials form a major class of molecular sieves[1] and are potentially useful in composite materials in sensor devices and as slow-release reagents. In a recent communication[2] we indicated that a monomer with two amine groups could be intercalated as a monolayer into α-tin hydrogen phosphate. Until now it has not been possible to prepare bilayers of bisamines as the two basic groups bind either to acid sites of the phosphate groups within the same layer or to those on adjacent layers. It is well known that layer mineral phosphates such as the above can be dissolved in aqueous solutions of the amines. This dissolution is probably due to the successive intercalation of the amines which separates the layers until the layer structure is lost. It was postulated that this dissolution process could be interrupted to form bilayers of bisamines by suitable choice of the amine and of the solvent used for the amine. Previous studies[3,4] with 1,4-diazabicyclo[2.2.2]octane (triethylenediamine or DABCO) have not led to bilayers. However, DABCO was thought to be suitable for this purpose because its bulky shape prevents orientation parallel to the phosphate layers. The free area of each active site in α-$Sn(HPO_4)_2\cdot H_2O$ is approximately 21.4 Å^2 whereas the cross-sectional area of DABCO is 28 Å^2. Although DABCO is a strong base, it was considered possible that the stereochemical restriction of the availability of active sites might also encourage bilayer formation. These figures compare with 23.99 Å^2 for the free area[5] of each active site in α-$Zr(HPO_4)_2\cdot H_2O$ which may also form bilayers.

Some *X*-ray diffraction data are given in Table 1 together with an outline of the method of preparation. When water was used as the solvent and there was a 3 : 1 molar excess of the base, the layer structure of the phosphate was destroyed and the phosphate was hydrolysed to a gel. However, with a 1 : 1 molar ratio using water as solvent (sample 2) clear peaks were seen at 7.85 Å (the α-tin phosphate) and 10.84 Å (monolayer) with a second order band at 5.45 Å. This sample had the approximate composition of $Sn(C_6H_{12}N_2)_{0.12}(HPO_4)_2\cdot 1.25H_2O$. Much the same was observed for sample 3 (molar ratio 0.5 : 1). There were no signs of multiple layer formation when water was used as solvent.

When the solvent was changed to toluene, however, there were clear indications of multiple layer formation. For example, when the molar ratio was 3 : 1 (DABCO : α-tin phosphate) there was no peak at 7.85 Å but there were clear peaks at 16.82 Å (with second order at 8.49 Å) and one at

Table 1. Data for DABCO and α-$Sn(HPO_4)_2{\cdot}H_2O$ compounds.

Sample	Molar ratio DABCO : phosphate	Solvent (pH_1pH_2) (start, finish)	*X*-Ray data/Å	Differential thermal analysis/K
1	3 : 1	H_2O (9.7, 7.9)	Destroyed	
2	1 : 1	H_2O (9.4, 7.0)	7.85; 10.84; 5.4 (second order)	329, endo; 403, endo; 613, exo; 770, endo
3	0.5 : 1	H_2O (9.1, 6.9)	7.85; 10.84; 5.4 (second order)	
4	3 : 1	Toluene	16.99; 11.48; 8.49 (second order)	344, endo; 373, endo; 673, exo; 828 exo
5	1 : 1	Toluene	16.82; 10.96; 7.8 (very weak)	344 endo; 373, endo; 673, exo; 828, exo
5(II)	1 : 1	Sample 5 heated to 383 K	16.08; 11.01	
6	0.5 : 1	Toluene	7.8	

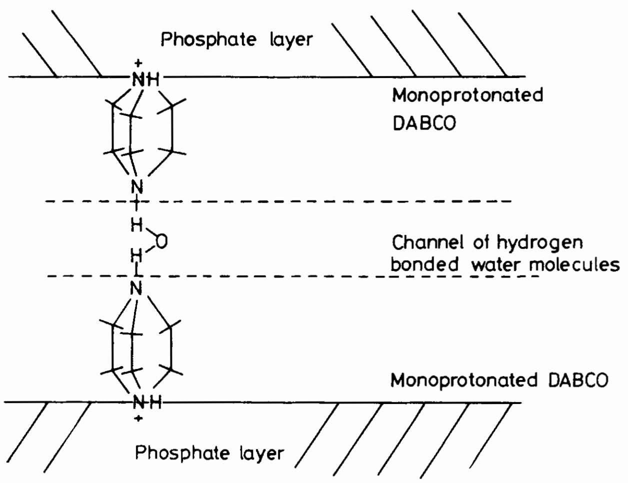

Figure 1. Idealised arrangement of the DABCO bilayer before heating.

11.48 Å (monolayer). The diprotonated form of DABCO contributes[3,4] 5.5 Å to d-spacing in vermiculite and 4.6 Å in smectites. The value of 16.82 Å, therefore, approximates to a bilayer of DABCO. Owing to its bulky shape it is likely that DABCO is in the β- orientation[6] which means that it may lie almost perpendicular to the phosphate plane. The thermal analysis of this sample showed endotherms at 344 and 373 K; these are associated with loss of water and perhaps some amine[5] as butylamine starts to be lost from α-zirconium phosphate at *ca.* 410 K. Amine oxidation was at 673 K. There was conversion of orthophosphate to pyrophosphate at 828 K. There was no evidence of facile collapse of the bilayer. For example, sample 5 was heated to 383 K, cooled, and resubmitted for *X*-ray analysis. The d-spacing decreased slightly to 16.08 Å and the difference of 0.74 Å includes loss of hydrogen bonded water between the base groups. The peak at *ca.* 6.8 Å was always accompanied by one at *ca.* 11 Å. This is to say that bilayer formation was always accompanied by monolayer formation and it appears possible that either monolayer formation may indeed precede bilayer formation or there are separate regions of mono- and bi-layers. In the case where the molar ratio of DABCO : α-tin phosphate was 0.5 : 1 (sample 6) there was no reaction as the donor properties of the basic nitrogen group were lower in toluene than in water.

The most probable configuration of this bilayer is shown in Figure 1. The thermal analysis shows that the DABCO is strongly bound and protonated at the interfaces where it is bound to the phosphate groups. The unbound end of the DABCO is not protonated but may be hydrogen bonded like glycols by a water molecule. This molecule was possibly lost on heating to *ca.* 370 K. It has been shown[3] that an i.r. band at 1471 cm^{-1} is evidence of the diprotonated form of DABCO (in smectites) and one at 1463 cm^{-1} refers to the molecular form. When toluene was used as a solvent (samples 4, 5) there was one broader band at 1468—1472 cm^{-1}. The samples which had been heated had a clearer spectrum and the principal peaks were at 1463 and 1468 cm^{-1} with a shoulder at 1471 cm^{-1} which lends some support to the idealised structure proposed in Figure 1. The principal role of the hydrocarbon solvent appears to be to limit the extent of diprotonation of the amine which occurs in water since the diprotonated form on intercalation only forms monolayers. Once the intercalated water molecules have been removed the structure may tend to the bilayers formed by monoamines[5] in which there are hydrophobic interactions between the unbound ends of the amine. The structure[8] may also be similar to that of zirconium bis(benzene phosphate) in which the ends of the rings approach but do not overlap.

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