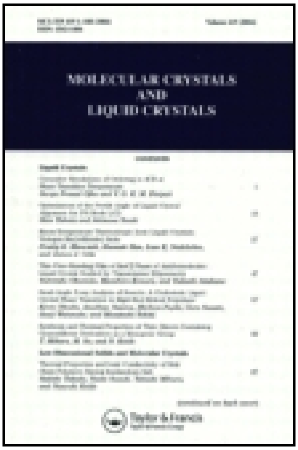

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Intercalation of Hydrazine and Amines in Antimony Phosphate

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INTERCALATION OF HYDRAZINE AND AMINES IN ANTIMONY PHOSPHATE

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Abstract The layered compound $SbPO_4$ has been intercalated with hydrazine, methylhydrazine and various amines at room temperature, either from solutions or vapor phase. The guest molecules form bilayers between the $SbPO_4$ layers.

INTRODUCTION

Intercalation of organic molecules in layered compounds has been the subject of many studies. The most thoroughly studied family of guest molecules is that of amines, including ammonia and hydrazine, while host compounds were generally[1-5] oxides, chalcogenides or phosphates such as $KTiNbO_5$, Ta_2NiS_5, α-$Sn(HPO_4)_2.H_2O$, $VOPO_4.2H_2O$, $NbOPO_4.3H_2O$.

In our search for new host structures in intercalation chemistry, we noticed that antimony phosphate, $SbPO_4$, has a layered structure[6,7] which could give rise to intercalation compounds. The unit cell is monoclinic, with the parameters a= 5.088 Å, b=6.762Å, c= 4.724 Å et ß= 94.64 °.

The $SbPO_4$ molecules form sheets built up of PO_4 tetrahedra and SbO_4 polyhedra sharing corners. The sheets extend parallel to the (bc) plane and are bound in the third direction by Van der Waals forces. Thus, $SbPO_4$ appears to be a good candidate as a host structure for intercalation.

Indeed, we show in this paper that $SbPO_4$ can be easily intercalated with hydrazine, hydrazine derivatives and amines at room temperature, either from solutions or vapor phase.

SYNTHESIS AND CHARACTERIZATION

$SbPO_4$ has been prepared from Sb_2O_3 by two routes. In the first one, Sb_2O_3 was allowed to react with an aqueous solution of H_3PO_4 by refluxing at 120°C during two days. The suspension was then filtered, washed thoroughly with water and dried. In the second method, a powder mixture of Sb_2O_3 and $(NH_4)_2HPO_4$ in stoichiometric amounts was heated overnight at 300°C, then ground and heated at 600°C during 3 days. Both methods gave products with X-ray diffraction spectra characteristic of pure antimony phosphate.

Intercalation attempts have been performed with the following compounds: hydrazine, methylhydrazine, ethylenediamine, 1,3-diaminopropane, isopropylamine, N-isopropylmethylamine, N,N,N',N'-tetramethylethylenediamine and methylamine. The reactions were carried out at room temperature, either in gaseous phase, by suspending a sample of $SbPO_4$ in the vapor of the compound to be intercalated, or from the liquid phase or appropriate solutions (soaking times: 2-7 days). In the latter case, the products were washed with water and dried before X-ray diffraction experiments. The vapor phase method, convenient for solutions with high vapor pressure at room temperature, was used for hydrazine, methylhydrazine, ethylenediamine and 1,3-diaminopropane. The phosphate sample placed in a Teflon holder was suspended to a calibrated quartz spring whose elongation gave the weight uptake as a function of time.

The density of the intercalated compounds was measured by helium pycnometry at room temperature using a Micrometric apparatus.

EXPERIMENTAL RESULTS

Figure 1 gives the X-ray spectra obtained before and after intercalation of $SbPO_4$ with the different molecules. The spectra are quite similar, exhibiting a new set of peaks. However for isopropylamine (IPA), N-isopropylmethylamine (N-IPMA), tetramethylethylenediamine (TMED) and methylamine (MA), the peaks of the pristine phosphate are still present, indicating an incomplete reaction (spectra 1f to 1h). However it may be possible to increase the intercalation level by changing the reaction conditions. For example, intercalation attempts performed at 40°C for MA (liquid phase) resulted in an intercalation compound with only traces of pristine phosphate (spectrum 1i).

Whatever the intercalation method (from liquid or vapor phase), identical spectra were obtained. This was also the case for hydrazine (HYD) (spectrum 1b), where, in addition, water solutions were used with different HYD concentrations. It must be noticed that reaction with HYD solutions produced gas bubbles, as generally observed with other systems[3]. Nevertheless, by heating at 600°C under vacuum, the pristine phosphate

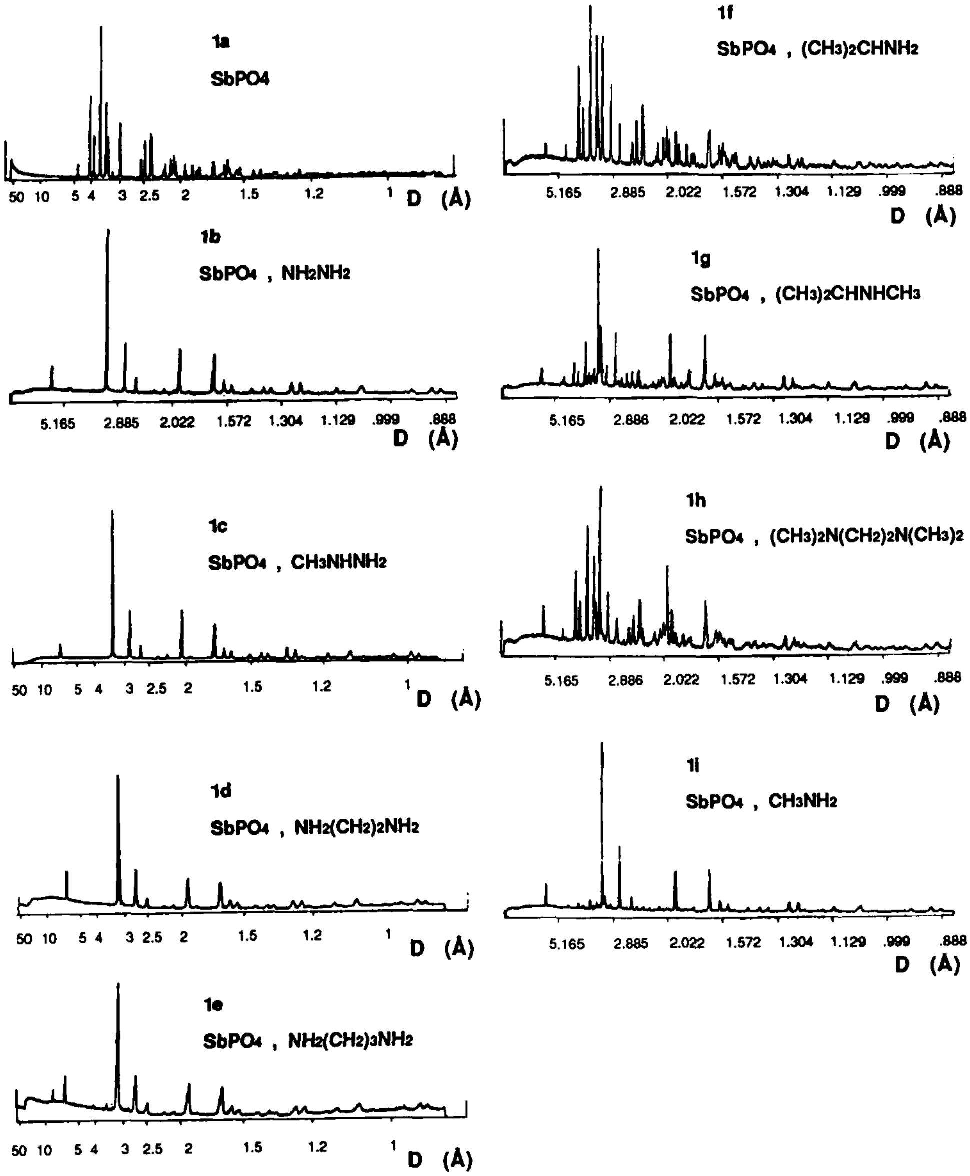

Figure 1: X-ray diffraction patterns of $SbPO_4$ and its intercalation compounds

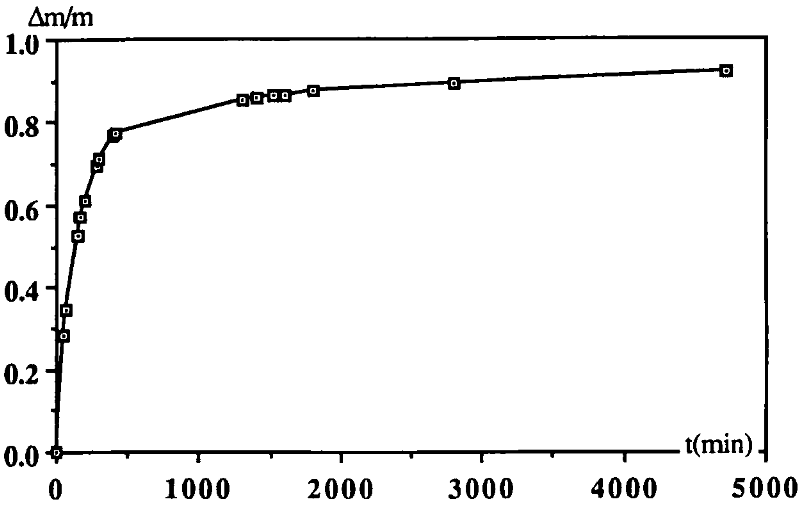

Figure 2: Time dependence of the weight uptake of a $SbPO_4$ sample submitted to hydrazine vapor at room temperature.

was restored, as shown by X-ray diffraction. The reversibility of the reaction indicates that an intercalation compound was formed.

Figure 2 shows the weight uptake as a function of time observed during intercalation of HYD from vapor phase. It can be noticed that 83% of the weight uptake occurs during the first 400 minutes for a total duration of about 5000 minutes. The intercalation compound obtained at the end of the reaction exhibited the same X-ray spectrum as those obtained from solutions.

The diffraction peaks of all spectra can be indexed with monoclinic unit cells, whose parameters b, c and ß are close to those of pristine $SbPO_4$. Only the a-parameter increases, as it is expected for the intercalation of the molecules between the $SbPO_4$ layers. The results are shown in Table 1, which gives also the weight uptake for complete intercalation and the densities measured and calculated using the weight uptake and unit cell parameter values. A good agreement is observed.

DISCUSSION

Examination of Table 1 shows that the a-parameter value is similar (≈12.7 Å) for all the intercalation compounds except DAP. The corresponding increase in interlayer distance is of the order of 7.6 Å. This value is close to the one observed[3] in the interca-

	Unit cell parameters(Å)			(°)	Density ± 0,02		
	a ± 0,04	b ± 0,02	c ± 0,02	ß ± 0,09	measured	calculated	Δm/m
Phosphate $SbPO_4$	5,088	6,762	4,724	94,64	4,37	4,45	
Hydrazine (HYD)	12,69	6,81	4,73	92,59	2,41	2,60	0,46
Methylhydrazine (MHYD)	12,7	6,76	4,73	93,12	2,25	2,59	0,52
Ethylenediamine (ETD)	12,69	6,73	4,74	92,99	2,31	2,36	0,33
1.3 diaminopropane (DAP)	16,22	6,74	4,76	92,81	2,32	2,33	0,68
Methylamine (MA)	12,66	6,71	4,66	94,83			
isopropylamine (IPA)	12,64	6,72	4,73	93,02			
N-isopropylmethylamine (N-IPMA)	12,59	6,71	4,75	93,91			
N,N,N',N'-Tetrametylethylenediamine (TMED	12,62	6,73	4,75	93,25			

Table 1: Unit cell parameters, densities measured and calculated, and weight uptake of $SbPO_4$ intercalation compounds with the listed molecules.

lation compound of HYD and diaminoethane in Ta_2NiS_5 . It is almost twice the length of the HYD molecule, which means that the intercalated layers are actually bilayers, with some tilting angle of the HYD molecules with respect to the host layers, which could be estimated to be about 60°. Such bilayers made up of tilted molecules have been observed[5], for example, in the intercalation of $VOPO_4$ and $NbOPO_4$ by aliphatic amines.

On the other hand, the maximum weight uptake would correspond to 3 HYD molecules per $SbPO_4$ molecule, if we assume that the intercalated species are NH_2-NH_2 molecules. This would lead to 6 HYD molecules per unit cell, which is impossible taking into account the available surface area in the (bc) plane and the molecular packing of HYD. However, if it is assumed that the intercalated species are hydrazine monohydrate, the weight uptake gives 4 molecules per unit cell, which can then be accommodated in the available space.

For the intercalation compounds with MHYD and DAP, the weight uptake values lead to 4 molecules per unit cell, whereas 2 molecules of ETD would be intercalated per unit cell. For these and the other investigated molecules we must also assume the existence of bilayers and variable tilting angles (up to 45°) in order to account for the a-parameter values. More structure work is needed to clear up this matter.

Finally, it must be noticed that molecules with two terminal N-H groups are more easily intercalated (HYD, MHYD, ETD and DAP). The other molecules give mixtures of non-intercalated and intercalated phosphate or require higher reaction temperatures, as indicated above for MA. It would be interesting to investigate the intercalation of other mono- and diamines to confirm this point.

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