Intercalation of Alkylamines into Tin(IV) Bis(hydrogenphosphate) Monohydrate

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Alkylamines have been intercalated into $Sn(HPO_4)_2 \cdot H_2O$ by exposing the phosphate to the vapour or the pure liquid of the amines. n-Alkylamines are intercalated as a bimolecular film of extended molecules with the carbon chain backbone roughly inclined at 66° to the plane of the sheet. Infrared spectra and thermal data suggest that the alkylamines exist as alkylammonium ions within the layer of $Sn(HPO_4)_2 \cdot H_2O$. The intercalate $Sn(C_4H_9NH_2)_2(HPO_4)_2 \cdot H_2O$ readily exchanges transition-metal ions.

Crystalline tin(IV) hydrogenphosphate, $Sn(HPO_4)_2 \cdot H_2O$, hereafter denoted as α-SnP, possesses a layer structure (interlayer distance 7.8 Å) similar to α-ZrP.[1] The ion-exchange properties of α-SnP with alkali-metal ions were investigated previously.[2-4] While the intercalation behaviour of α-ZrP toward amines has also been extensively investigated,[5-7] little is known about the intercalation behaviour of α-SnP.[8] The present paper describes the preparation of intercalation compounds of tin(IV) hydrogenphosphate with alkylamines, and also some thermoanalytical investigations.

Experimental

All the chemicals were of reagent grade and used without further purification. Microcrystals of $Sn(HPO_4)_2 \cdot H_2O$ were prepared according to the precipitation method of Costantino and Gasperoni.[2] Intercalation compounds with n-butylamine, n-pentylamine, isobutylamine, and s-butylamine were obtained by placing the phosphate in an atmosphere saturated with amine vapour at room temperature for 2 d. Intercalation compounds with n-hexylamine and n-heptylamine were prepared by equilibrating the host compound with the pure liquids at room temperature for 4 d. The solids were then separated by centrifugation. All intercalated samples were air dried, evacuated, and stored in a desiccator over a solution of 50% H_2SO_4 to eliminated superficially adsorbed amine.

Analyses.—The solids were analyzed for N by the micro-Kjeldahl method. Thermogravimetric and differential thermal analyses were carried out using a Rigaku-Thermoflex unit and a heating rate of 10 °C min^{-1}. Calcium oxalate was employed as a standard. *X*-Ray films were obtained on a Siemens-Kristalloflex 810 using nickel-filtered Cu-K_α radiation. The interlayer spacing of the intercalation compounds was calculated from the average of the first three-order reflections of the 002 plane. Infrared studies were carried out on a Beckman spectrophotometer by the KBr disc method.

Results and Discussion

The intercalation of alkylamines into α-SnP occurs at room temperature upon placing the phosphate in contact with the vapour, or the pure liquid, of the amine to be intercalated.

X-Ray films showed that the intercalates maintain their crystallinity. Reflections corresponding to the 002 and higher harmonics (004, 006) were observed. The original reflections due to the 112 and 202 planes were no longer seen. However, those due to the 110, 200, 020, and 220 planes remained but with lower intensities. The Table lists the interlayer distances and compositions of the alkylamine intercalates obtained from α-SnP. n-Alkylamines form stoicheiometric compounds containing 2 mol of amine per mol of α-SnP, and one molecule of water. The interlayer distances increase linearly with the number of carbon atoms in the alkyl chain. The slope of this dependence, $\Delta d/\Delta n_c = 2.32$, was computed by regression analysis. Assuming a *trans-trans* alkyl-chain conformation, this value indicates that n-alkylamines form a double layer of molecules inclined at an angle $\alpha = \sin^{-1}(2.32/2.54) = 66.0°$ with respect to the sheet. Using these results, the interlayer distance for the octylamine intercalate was found to agree closely with the value observed by Michel and Weiss[8] (28.8 Å).

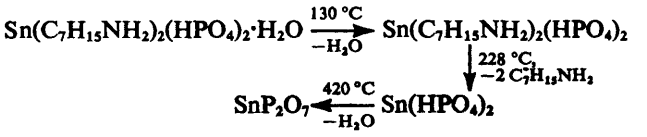
Table. Interlayer distance and composition of intercalation compounds of α-$Sn(HPO_4)_2 \cdot H_2O$ with alkylamines

Amine	Interlayer distance (Å)	Composition (mol amine per mol α-SnP)
n-Butylamine	19.5	2.0
n-Pentylamine	22.0	2.0
n-Hexylamine	23.9	1.9
n-Heptylamine	26.6	2.0
s-Butylamine	16.5	1.8
Isobutylamine	17.8	2.0

s-Butylamine and isobutylamine also form a double layer of amine occupying the space within α-SnP sheets. The intercalate isobutylamine–α-SnP has a larger interlayer distance than does s-butylamine–α-SnP. This fact may be explained if the branch at the end of the isobutylamine chain is considered.

In n-alkylamine–α-ZrP intercalates, Clearfield and Tindwa[7] assumed that the NH_2 group is engaged in a symmetrical hydrogen bond with adjacent POH groups, and they reported that the *trans-trans* alkyl formed a 60° angle with the sheets. However, the i.r. spectra of the n-alkylamine–α-SnP intercalates show bands at ν(N–H) 3 160s, $\delta(NH_3)^+$ 1 640m and 1 545m cm^{-1}, which suggest the existence of n-alkylammonium between the layers.

α-SnP, owing to the shorter product *ab*, should show a greater steric hindrance to the intercalation of alkylamines, and a larger packing density (4.7 alkyl chains per 100 $Å^2$) than α-ZrP (4.2 alkyl chains per 100 $Å^2$), thus avoiding the formation of kink and gauche defects[9] in the bilayer. So, the



Scheme. The temperatures shown are those corresponding to d.t.a. peaks

inclination angle of the n-alkylamine with the sheets is larger in the α-SnP intercalates than for corresponding α-ZrP, γ-ZrP, and γ-TiP intercalates which possess smaller packing densities than α-SnP.[10-13]

The data from the thermal studies were almost identical for all alkylamine–α-SnP intercalates. These compounds decomposed in three stages: dehydration, loss of amine, and condensation of orthophosphate groups to pyrophosphate. A typical decomposition process for the alkylamine intercalates is shown in the Scheme, using $Sn(C_7H_{15}NH_2)_2(HPO_4)_2 \cdot H_2O$ as an example.

The thermogravimetric curves show three steps. The weight loss in the second stage agrees with the N analysis in all cases. The thermal behaviour of these intercalates is similar to that observed for alkylamine–α-ZrP intercalates.[7,14,15] In spite of the different boiling points of the alkylamines, the temperatures corresponding to the d.t.a. peaks were practically the same for each amine intercalate. The high temperatures observed suggest the existence of alkylammonium ions, ionically bonded to the sheet, and that hydrogen bonding has an insignificant role in this interaction.[15]

The intercalate $Sn(C_4H_9NH_2)_2(HPO_4)_2 \cdot H_2O$ readily exchanges highly hydrated cations such as Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} when the corresponding acetates are employed in aqueous media.[16] This also indicates that the alkylamines are present as alkylammonium ions.

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