

NEW INTERCALATED COMPLEXES OF MPS_3 (M=Mg, Zn, Mn) WITH n-ALKYLAMINES

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New types of intercalated complexes are synthesized by the reaction of MPS_3 layer crystals (M=Mg, Zn, Mn) with n-alkylamines ($C_nH_{2n+1}NH_2$, n=1-8). The amines are adsorbed on the interlamellar surfaces of the MPS_3 crystals to form two different types of complexes of increased values in basal spacing. The spacing value of the first type of complexes is independent of the number of carbon atoms in alkyl chain of the amines, and the value of the second type of complexes increases with the number of the carbon atoms. The possible arrangements of the amines in the interlayer region are proposed for these types of complexes.

Extensive studies have been accumulated for intercalated organic complexes of layer silicate minerals such as montmorillonite and vermiculite. Recently, some other inorganic compounds of layer structures were found to adsorb various organic molecules on the interlamellar surfaces and to form intercalated organic complexes. Attention has been much increased onto the general area of intercalated complexes, since the electrical properties of some transition metal chalcogenides¹⁾ and iron(III) oxychloride^{2,3)} were known to be greatly influenced by the adsorption of pyridine on these interlamellar surfaces. The present paper is to report on the synthesis of new intercalated organic complexes of MPS_3 layer crystals.

In the crystals of MPS_3 , two-dimensional sulfide layers are bound together into stacks^{4,5)}. The adjacent two layers are only weakly interacted with van der Waals force of the interlayer S---S. It is expected, therefore, that some organic molecules can be adsorbed in the interlayer region to form intercalated complexes. The structure of the sulfide layer in MPS_3 can be related to that of the chloride layer in $CdCl_2$. The chloride layer results in the sulfide layer when two-thirds of Cd cations are replaced with divalent cations, and the rest of Cd positions are occupied by P-P pairs and all the Cl anions are replaced with S anions.

Three kinds of MPS_3 layer crystals (M=Mg, Zn, Mn) used in the present investigation were prepared by heating the constituent elements in evacuated and sealed silica glass tubes. The reaction condition, the basal spacing and the color of the crystals are listed below. The intercalated complexes with n-alkylamines ($C_nH_{2n+1}NH_2$, n=1-8) were synthesized by dispersing MPS_3 crystals in the amine liquids at 30°C for 3 days. Methyl- and ethyl-amines were used as the aqueous solutions of about 10 M concentration. After withdrawal out of the amines, the crystals were

MPS ₃	reaction temp. T/°C	duration t/week	basal spacing d/Å	color
MgPS ₃	650	2	6.50	colorless
ZnPS ₃	490	1	6.46	light yellow
MnPS ₃	680	2	6.49	green

observed on the basal spacings by an X-ray diffractometer using Cu-K α radiation. The change in basal spacing of the crystals was observed again after the removal of the amines extractable by rinsing the crystals with acetone.

Fig. 1 shows the plot of the observed basal spacing values against the number of carbon atoms in n-alkyl chains. The complexes of MgPS₃ and ZnPS₃ with a given amine except for n-octylamine have respectively a single basal spacing which increases linearly with the number of carbon atoms. These complexes exhibit no change in basal spacing by the acetone rinse. On the other hand, the complex of MnPS₃ is a mixture of phases with different basal spacing values. One of the values is similar to those of the corresponding complexes of MgPS₃ and ZnPS₃. On rinsing with acetone, all the spacing values of the complexes of MnPS₃ reduced to about 10.5 Å, irrespective of the length of the amine chains.

The amount of n-butylamine adsorbed on MnPS₃ at room temperature was determined

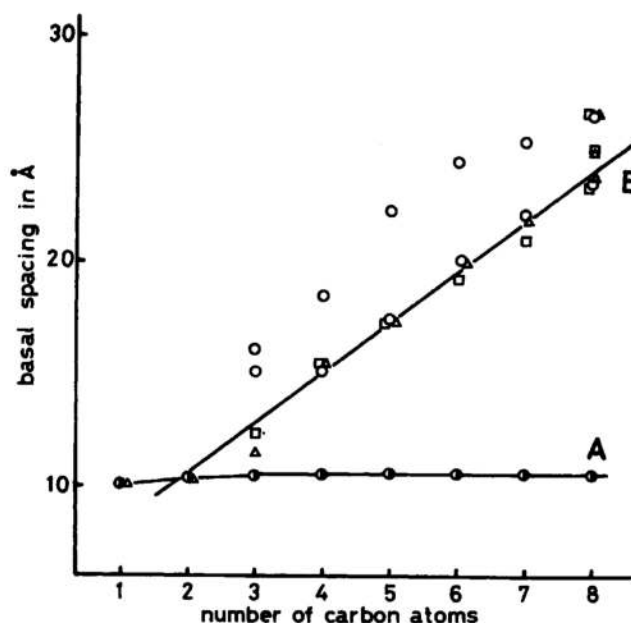


Fig. 1. Basal spacing of the n-alkylamine complexes of MPS₃ against the number of carbon atoms in the amine chains.

○ and ● : observed for MnPS₃ after it was withdrawn out of liquid amines, and then after rinsing with acetone, respectively.

□ and △ : observed for MgPS₃ and ZnPS₃ after they were withdrawn out of liquid amines, respectively. The complexes of MgPS₃ and ZnPS₃ exhibited no change in basal spacing on rinsing with acetone.

gravimetrically. The amine vapor from a liquid n-butylamine bath was introduced into an evacuated cell, in which MnPS_3 was kept in a quartz vessel suspended with a quartz spring balance. The temperature of the amine bath was kept lower than room temperature by 5°C to prevent the condensation of the amine vapor on the crystal surfaces. The amount of adsorption of the amine vapor was determined by measuring the extension of the balance until the equilibration at room temperature was attained after 3 days. The adsorption curve showed that MnPS_3 reacted with the amine to form the complexes $\text{MnPS}_3 \cdot 1/3\text{C}_4\text{H}_9\text{NH}_2$ (I) in the first stage, $\text{MnPS}_3 \cdot 1/2\text{C}_4\text{H}_9\text{NH}_2$ (II) in the second stage and to result in the complex of the composition near $\text{MnPS}_3 \cdot \text{C}_4\text{H}_9\text{NH}_2$ (III) in the final stage. The desorption curve on evacuation after the above determination indicated that the complex (III) was reversibly changed to the complex (II). The latter complex showed no change in composition on the prolonged evacuation and also on the heat treatment up to 100°C . The basal spacing of the complex (II) was observed to be 10.5 \AA , in accordance with that of the complex after the removal of the acetone-extractable amine. Similar adsorption study of n-butylamine on MgPS_3 and ZnPS_3 revealed that each of them formed the complex of a composition $\text{MgPS}_3 \cdot \text{C}_4\text{H}_9\text{NH}_2$ and $\text{ZnPS}_3 \cdot \text{C}_4\text{H}_9\text{NH}_2$, respectively, and that these complexes were stable against prolonged evacuation unlike the complex (III) of MnPS_3 . This finding is compatible with the fact that the complexes of MgPS_3 and ZnPS_3 with n-butylamine had a single basal spacing.

These results suggest the presence of two types of complexes depending on the arrangement of the molecules adsorbed on the interlamellar surfaces of MPS_3 . The complexes of the first type, called hereafter Type A, are those of 10.5 \AA basal spacing independent of the length of n-alkyl chains, which are obtained by the reaction of MnPS_3 and n-alkyl amines followed by rinsing with acetone. Since the thickness of a sulfide layer in MnPS_3 is 6.5 \AA which includes the van der Waals radius of sulfur on each side of the layer, the increase in basal spacing on the complexation of MnPS_3 with the amines is 4.0 \AA . This increase is in accordance with the van der Waals diameter of a CH_3 group. Thus, the alkyl chains must be arranged parallel to the sulfide layers in the complexes of Type A.

The complexes of the second type (Type B) are those of basal spacings increasing with the number of carbon atoms in the alkyl chains. There exists a linear relationship between the basal spacing and the number of carbon atoms in this type of complexes, as previously shown in Fig. 1. The slope of the straight line shown in the figure is about 2.5 \AA per carbon atom, which is twice the increase (1.27 \AA) in the length of an alkyl chain per carbon atom. This finding can be explained by a double layer of fully extended amine molecules standing almost perpendicular to the sulfide layers. However, the basal spacings calculated on this amine arrangement are much larger than those observed:

$$d_{\text{calcd.}} = (\text{thickness of sulfide layer}) + 2 \cdot [(\text{length of carbon chain}) + (\text{N-C distance}) \cdot \sin 54.73^\circ + (\text{van der Waals radius of } \text{NH}_2) + (\text{van der Waals radius of } \text{CH}_3)] = 6.5 + 2 \cdot [(n-1) \cdot 1.27 + 1.25 + 1.5 + 2.0] = 16.0 + (n-1) \cdot 2.54 [\text{\AA}], \quad (n: \text{number of carbon atoms})$$

$$d_{\text{obs.}} = 10.5 + (n-2) \cdot 2.5 [\text{\AA}], \quad (n \geq 2)$$

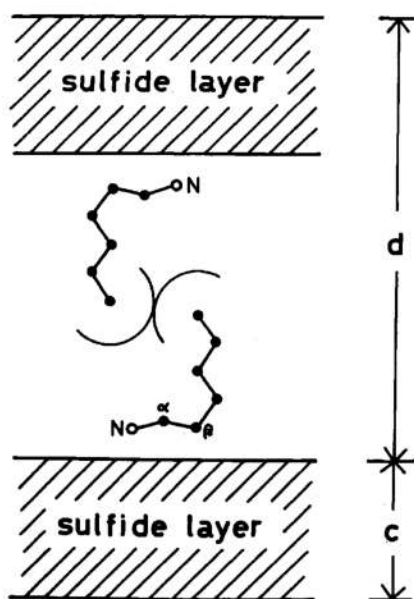


Fig. 2. Schematic representation of the double layer of *n*-alkylamine in the complexes of Type B.

- c: thickness of a sulfide layer
d: basal spacing of the complex

It is noteworthy that formations of alkyl chains in the *n*-alkylamine complexes of MPS_3 and TiS_2 are different, though these sulfides have similar interlamellar surfaces. The further study is under way in our laboratory on the effect of the cations within sulfide layers on the amine conformation of these complexes, and will be presented elsewhere.

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This discrepancy can be explained in terms of a variety of the conformations of the alkyl chains. It is not easy at the present stage of investigation to show the definite conformation of the alkyl chains in the complexes of Type B. One of the possible conformations is proposed in Fig.2, in which the α - and β -positioned carbon atoms in the alkyl chain are, similar to the case of the complexes of Type A, lying on the surface of the sulfide layer, and the rest carbon chain linking to the β -positioned carbon atom stands perpendicular to the layer. There are some other complexes of basal spacings larger than those of the complexes of Type B, as shown in Fig.1. The spacing in these complexes can be ascribed to some compromise conformation of alkyl chains.

Another layer structured compound TiS_2 also forms a series of complexes with *n*-alkylamines⁶). The alkyl chains in those complexes were reported to be fully extended and standing perpendicular to TiS_2 layers.