INTERCALATION OF ORGANIC MOLECULES INTO LAYERED PHOSPHATES -CORRELATION BETWEEN STRUCTURE AND FUNCTION-

Hirokazu Nakayama *

(*Corresponding author: hiro@kobepharm-u.ac.jp)

Department of Functional Molecular Chemistry, Kobe Pharmaceutical University, 4-19-1 Motoyamakitamachi,
Higashinada, Kobe, Hyogo 658-8558 Japan.

Keywords: Layered phosphate, Intercalation, Solid State NMR

Abstract: Precise investigation of intercalation compounds of layered phosphates by solid state NMR could explore the microscopic picture of intercalation phenomena. By ^{31}P solid state NMR experiment, type of layered phosphate and existence of various phosphates, H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} groups, can be distinguished. The microscopic picture of diethylenetriamine-intercalated α -zirconium phosphate, and its mechanism can be obtained by ^{13}C and ^{31}P solid state NMR. Furthermore, the adsorption of carboxylic acids by diethylenetriamine-intercalated α -zirconium phosphate and the exchange of methylene blue with butylamine in butylamine-intercalated α -zirconium phosphate can be clarified microscopically.

(Received December 12, 2008; Accepted January 26, 2009)

INTRODUCTION

Clearfield^{1,2} synthesized two different types of layered zirconium phosphates, α -Zr(HPO_4)₂·H₂O (α -ZrP) and γ -Zr(H_2PO_4)(PO_4)·2H₂O (γ -ZrP) in 1960s. These layered zirconium phosphates are insoluble acid salts, and are known as inorganic ion exchangers. Because α -ZrP and γ -ZrP have acidic protons, these protons can react with bases and cations. Therefore, they can readily intercalate various organic compounds, such as amines and quaternary ammonium ions. The extensive experimental studies on the preparation of intercalation compounds between these materials and various guest molecules have been done in 1970's³⁻⁸.

Recently, inorganic layered compounds, such as, layered clay and layered phosphate, have been attracted much attention as the hosts of inorganic-organic hybrid materials with new functions. Although the syntheses of these hybrid materials are simple, the resultant hybrid materials can obtain new function, which could not be possessed by inorganic host or organic guest alone.

It is important to obtain the molecular scale picture of hybrid material to understand its function and to know the guideline of the molecular design of the hybrid materials. However, it was rare to investigate the inorganic-organic hybrid materials by solid-state NMR, when I started our project in the middle of 1990s. The intercalation compounds were examined mainly by XRD and IR, and the information of molecular level was not enough at that time.

Therefore, we started the project to clarify the microscopic picture of the intercalation phenomena of layered phosphates and their functions by solid state NMR. This review consists of three sections, determination of the type of layered phosphate, intercalation mechanism and microscopic picture of intercalation compound of layered phosphate, and the correlation between structure and function.

STRUCTURE OF LAYERED PHOSPHATES

Figure 1 shows the crystal structures of α -ZrP and γ -ZrP. Although only the amount of water differs in α -ZrP and γ -ZrP, their structure and the physico-chemical properties are considerably different. For example, α -ZrP and γ -ZrP differ from each other in the capability of intercalating various guest molecules. In order to understand this different intercalation behavior between α - and γ -ZrP, Clearfield and his co-workers intensively tried to determine the crystal structure by X-ray diffraction and reported the crystal data of α -ZrP^{9,10}. In α -ZrP, each zirconium atom is octahedrally coordinated by six oxygens of six different phosphate groups. On the other hand, three oxygens of a phosphate group are coordinated to three zirconium atoms, and the fourth oxygen bonds with a proton and projects into the interlayer space. The water molecule in the interlayer space forms a hydrogen bond network with phosphate groups. And the interlayer distance is 0.76 nm. The position of hydrogen in α -ZrP was later determined by neutron diffraction experiment¹¹.

FIGURE 1 Structures of (a) $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and (b) $\gamma\text{-Zr}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$.

On the other hand, the crystal structure of $\gamma\text{-ZrP}$ was determined in 1995 by Rietveld method to the powder X-ray diffraction pattern¹². In $\gamma\text{-ZrP}$, each zirconium atom is octahedrally coordinated by six oxygens of phosphate group. There are two chemically different phosphate groups, that is, H_2PO_4 and PO_4 , in $\gamma\text{-ZrP}$. All oxygen atoms of PO_4 group are coordinated to zirconium atoms, whereas two oxygens of H_2PO_4 group bond acidic protons and project into the interlayer space, although the position of hydrogen was not determined. The water molecules in the interlayer space form a hydrogen bond network with phosphate groups. And the

interlayer distance is 1.22 nm.

In order to extend the field of intercalation chemistry of layered phosphate, the other layered phosphates of tetravalent metals, such as Ti(IV), Ce(IV), Sn(IV), Pb(IV) and Hf(IV), and those of trivalent metal, such as Al(III), have been found. Because it is difficult to obtain single crystal in these layered phosphates, the structural data were lacking. Structural data of various layered phosphates are summarized in Table 1. The crystallographic data of the layered Ti(IV), Ce(IV), and Al(III) phosphates have not yet been obtained in 1990s. Clayden proposed a method to distinguish three phosphate groups, H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} on the basis of ^{31}P CP/MAS spectra¹³. Although his method is powerful to determine the type of layered phosphate, it needs time-consuming experiment.

I proposed another conventional method and applied various layered phosphates. The ^{31}P MAS spectra of the Ti(IV) phosphates with and without ^1H high power decoupling are shown in Fig. 2¹⁴. The dipole-dipole interaction between ^1H and ^{31}P causes broadening of the ^{31}P signal considerably in the MAS

FIGURE 2 ^{31}P MAS NMR with (top) and without (bottom) ^1H high-power decoupling for (a) $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and (b) $\gamma\text{-Zr}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$.

TABLE 1 Structural data of layered phosphates

	d / nm	Structural Data
$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	0.756	X-ray (Rietveld 1968, 1977), Neutron (1977)
$\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	0.756	X-ray (Rietveld 1990)
$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot (\text{NaPO}_4) \cdot \text{H}_2\text{O}$		X-ray (Single, H position 1988)
$\gamma\text{-Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	1.220	X-ray (Rietveld 1995)
$\gamma\text{-Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	1.163	X-ray (Rietveld 1990, ?)
$\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$	1.607	(?)
$\text{AlH}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ (type I)	0.700	(?)

only spectrum. The ^1H high power decoupling technique diminishes this interaction and brings about a sharp resonance line as can be seen in Fig. 2. Hence one can distinguish protonated and unprotonated phosphates. The broad peak at -10 ppm in the spectrum of γ -TiP without ^1H decoupling indicates strong ^1H and ^{31}P dipole-dipole interaction. Therefore, the peaks at -10.8 and -33.0 ppm can be assigned to H_2PO_4^- and PO_4^{3-} , respectively. This assignment is also confirmed by the contact time dependence of CP/MAS spectra.

We applied the above method to the other

In the ^{31}P MAS spectrum of crystalline $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$, two peaks are observed at -10.6 and -28.3 ppm. The contact time dependence of CP/MAS spectra and MAS spectrum without ^1H decoupling imply that the peaks at -10.6 and -28.3 ppm are assigned to H_2PO_4^- and PO_4^{3-} , respectively. Although the crystal structure of $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ (CeP) is unknown, the existence of H_2PO_4^- and PO_4^{3-} suggests that it belongs to the γ -type of layered phosphates $\text{M}^{\text{IV}}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Zr}$ and Ti). The phosphate of the γ -type usually contains two waters of crystallization. Therefore, in CeP one third of water of crystallization is deficient. The

TABLE 2 ^{31}P chemical shift for layered phosphates

	$\delta_{\text{iso}}/\text{ppm}$	sites	
α -Zr $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	-18.7	$(\text{HPO}_4)^{2-}$	ref. 13
α -Ti $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$	-18.4	$(\text{HPO}_4)^{2-}$	this work
α -Zr $(\text{HPO}_4)(\text{NaPO}_4) \cdot \text{H}_2\text{O}$	-15.0	$(\text{NaPO}_4)^{2-}$	this work
	-17.3	$(\text{HPO}_4)^{2-}$	
γ -Zr $(\text{HPO}_4)_2 \cdot 2 \text{H}_2\text{O}$	-9.4	$(\text{H}_2\text{PO}_4)^-$	ref. 13
	-27.4	$(\text{PO}_4)^{3-}$	
γ -Ti $(\text{HPO}_4)_2 \cdot 2 \text{H}_2\text{O}$	-10.6	$(\text{H}_2\text{PO}_4)^-$	this work
	-32.6	$(\text{PO}_4)^{3-}$	
γ -Ce $(\text{HPO}_4)_2 \cdot 1.33 \text{H}_2\text{O}$	-10.6	$(\text{H}_2\text{PO}_4)^-$	this work
	-28.3	$(\text{PO}_4)^{3-}$	
$\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2 \text{H}_2\text{O}^{\text{a)}}$	-20.8	$(\text{HPO}_4)^{2-}$	this work
	-22.9	$(\text{HPO}_4)^{2-}$	

layered phosphates. The measured chemical shift values and their assignments to the specified phosphate ions are summarized in Table 2. δ_{iso} of α -TiP and γ -TiP are close to those for the corresponding layered zirconium phosphates, α -ZrP and γ -ZrP, respectively. α -TiP¹⁵ is found to be isomorphous to α -ZrP and to contain HPO_4^{2-} group in the structure. Two compounds, γ -ZrP and γ -TiP, are found to be isomorphous from XRD data [20], although the crystal structure of γ -TiP has not yet been solved.

Alpha-form of layered phosphate has one kind of phosphate group, HPO_4^{2-} , whereas γ -form of layered phosphate has two chemically different kinds of phosphate groups, PO_4^{3-} and H_2PO_4^- ^{10,12}. These three types of phosphate groups in layered zirconium and titanium phosphates have characteristic chemical shift values as shown in Fig. 3¹⁴. The chemical shift values of H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} groups are about -10, -20, and -30 ppm, respectively. And the signals for γ -form appear at around -10 and -30 ppm with equal intensity. Therefore, type of phosphate group in layered phosphate, and structural type, that is, α - or γ -type, can be classified by ^{31}P isotropic chemical shift values as well.

lack in water of crystallization may fulfill an important role to produce a large difference in the structure and the bonding characteristics of H_2PO_4^- and PO_4^{3-} groups. Layered cerium phosphates are reported to have many polymorphic forms, $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$ and 2), depending on the number of hydration water¹⁷.

The ^{31}P NMR spectrum of $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$

FIGURE 3 ^{31}P NMR chemical shift values of various layered phosphates

(AIP) has three peaks at -20.8, -22.9, and -29.6 ppm, suggesting that the structure of layered aluminum triphosphate is completely different from those of

layered zirconium(IV), titanium(IV), and cerium(IV) phosphates. In $M^{IV}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $M^{IV}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ($M = \text{Zr, Ti, or Ce}$) mentioned above, each PO_4^{3-} is isolated from each other and coordinates individually to the metal atom. On the other hand, three phosphate groups in AIP form a triphosphate ions $\text{P}_3\text{O}_{10}^{5-}$ with the P-O-P-O-P bond by sharing apical oxygens of three PO_4 groups. The contact time dependence of CP/MAS spectrum indicates the existence of a weak dipole-dipole interaction between ^1H and ^{31}P for the peak at -29.6 ppm. The other two peaks in the ^{31}P MAS spectrum are very broad when the ^1H high power decoupling is absent. These facts suggest that the peaks at -20.8 and -22.9 ppm are assigned to the end HPO_4^{2-} groups of triphosphate anion, and the peak at -29.6 ppm to middle PO_4^{3-} group.

Therefore, our proposed method using ^{31}P solid-state NMR is the powerful tool to determine the structural type of layered phosphate.

INTERCALATION OF LAYERED PHOSPHATES

We found that the structural information of layered phosphate could be obtained by solid state ^{31}P NMR. Then we shifted to examine the intercalation compound of layered phosphate to elucidate the microscopic picture of intercalation compound. In this section diethylenetriamine-intercalated α -ZrP is shown as an example.

Two kinds of diethylenetriamine (2E3A) intercalation compounds with different interlayer distances could be obtained for α -zirconium phosphate¹⁸. On increasing the concentration of 2E3A aqueous solution, the diffraction peak of the host α -ZrP ($d = 0.75$ nm) disappeared completely within 30 min and the peak of Phase I ($d = 1.02$ nm) was observed. Then, Phase I transformed slowly to Phase II ($d = 1.58$ nm), and a pure Phase II was obtained after 7 d. The uptakes of 2E3A into α -ZrP were 1.5 and 2.7 $\text{mmol} \cdot \text{g}^{-1}$ of α -ZrP for Phase I and Phase II, respectively. The ratio of two phases changed on the reaction time. In order to determine the transformation rate from Phase I to Phase II quantitatively, a first-order reaction equations were applied, and the transformation rate was estimated to be $7.7 \times 10^{-2} \text{ h}^{-1}$. Furthermore, in order to determine the transformation enthalpy, temperatures dependence experiment was performed. From the plot of $\ln k$ vs. $1/T$ the enthalpy of phase transformation is calculated to be $30 \text{ kJ} \cdot \text{mol}^{-1}$.

In order to clarify the interaction between the α -ZrP layer and 2E3A molecule microscopically and

also to understand the origin of the transformation enthalpy, the ^{31}P MAS NMR spectra were measured for 2E3A intercalation compounds of α -ZrP (Fig. 4)¹⁹. It is known that the host α -ZrP has only one kind of phosphate group, HPO_4 , and that the signal of HPO_4 group is appeared at -18.7 ppm (Fig. 4-(8))¹⁴. On intercalating 2E3A into α -ZrP, this peak gradually moves to a low field to -15.7 ppm. Morgan *et al.* reported that the peaks of the alkylamine intercalation compounds of α -ZrP shift by +3.7 ppm from that of host α -ZrP (-18.7 ppm) in ^{31}P MAS NMR spectra because of the deprotonation of phosphate group ($-\text{P}-\text{OH} \rightarrow -\text{P}-\text{O}^- \cdots \text{H}_3\text{N}^+$)^{20,21}. It suggests that all the phosphate groups of α -ZrP interact with amino group of 2E3A in a same way. On the contrary, the peak of phosphate group in Phase I (Fig. 4-(7)) shifted scarcely and was broad, because the interaction between phosphate group and 2E3A is weak and several different environments of phosphate groups exist. Therefore, the interaction between the host α -ZrP and 2E3A is considerably different for two phases.

FIGURE 4 Reaction time dependence of ^{31}P MAS NMR spectra of 2E3A-intercalated α -ZrP. (1) 7 d, (2) 1 d, (3) 15 h, (4) 5 h, (5) 3 h, (6) 1 h, (7) 30 min, (8) 0 (α -ZrP)

The conformations of 2E3A in the interlayer regions of Phase I and Phase II estimated from XRD and ^{31}P and ^{13}C NMR are shown in Fig. 5. In Phase II the uptake of 2E3A (2.7 mmol / g) is half of

FIGURE 5 Schematic structural models of Phase I (left) and Phase II (right)

maximum intercalation capacity of α -ZrP. This means that almost all HPO_4 sites interact with two terminal amino groups of 2E3A molecule in a same way (Fig. 5-(b)). This is reflected in a sharp ^{31}P signal at -15.7 ppm. As the van der Waals length along the long axis of 2E3A molecule with *all trans* form is $8.9 \text{ \AA}$, the expansion of the interlayer distance by $8.2 \text{ \AA}$ supports above model. The transformation enthalpy from Phase I to Phase II, 30 kJ , is comparable with the barrier of internal rotation from *cis* form to *trans* form. Therefore, in Phase I, 2E3A molecules exist in bent form with 180 degree rotation against the bond between secondary amino group and its adjacent carbon atom. And the phosphate groups interact with amino groups of 2E3A weakly and several different kinds of phosphate sites existed. This is reflected in broad ^{31}P signal. Furthermore, the expansion of the interlayer distance by 0.26 nm , is reasonable, because the size of 2E3A molecule with a bent form is 0.34 nm .

In this way, the microscopic intercalation scheme can be estimated by solid state NMR. The intercalation schemes of α,ω -alkanediamine intercalation compounds of AlP^{22} , and *n*-alkylamine intercalation compounds of CeP^{23} , that is, $\gamma\text{-Ce}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 1.33\text{H}_2\text{O}$ ($\gamma\text{-CeP}$) could also be elucidated by ^{13}C and ^{31}P solid-state NMR in a similar way.

FUNCTION OF MODIFIED LAYERED PHOSPHATES

We found that the microscopic picture of the intercalation compound of layered phosphate can be elucidated by solid state NMR. In the next stage we examined the microscopic picture of the function of intercalation compound of layered phosphate. In this section I introduce adsorption properties of diethylenetriamine-intercalated α -ZrP and pillar method of butylamine-intercalated α -ZrP as examples.

The time dependence of the adsorption amounts of carboxylic acids for 2E3A-intercalated α -ZrP are shown in Fig. 6. For Phase I, except for formic acid, the adsorption amounts of the carboxylic acids were less than 10% . On the other hand, Phase II adsorbed gaseous carboxylic acids with more than 30% increases in the overall weight of the intercalation

FIGURE 6 Time dependence of the adsorption amounts of (a) formic acid, (b) acetic acid, (c) propionic acid, and (d) butyric acid: Phase I (●), and Phase II (□)

compounds, implying the adsorption of one carboxylic acid molecule per one polyamine molecule. Following the adsorption of gaseous carboxylic acid, the interlayer distances (d) of Phase II increased linearly with longer alkyl length (n) whereas no change in Phase I. The systematic expansion of the interlayer distances implied that the adsorption of the carboxylic acid molecules resulted in their co-intercalation within the interlayer spaces of Phase II.

^{31}P MAS NMR spectra following the adsorption of carboxylic acids are shown in Fig. 7. In the case of Phase I, the NMR spectra remained unchanged following the adsorption of carboxylic acid gases; this was reasonable and consistent with the results of uptake and XRD, which show that Phase I adsorbed only a few carboxylic acids. On the other hand, drastic changes in the NMR spectra were observed for Phase II. For Phase II, before the introduction of the carboxylic acids, the two terminal amino groups

FIGURE 7 ^{31}P MAS NMR spectra of (a) Phase I and (b) Phase II before and after maximum adsorption of the carboxylic acids. The values (%) are the increase in weight.

(1) Phase I, (2) HCOOH (40.7 %), (3) CH_3COOH (13.7 %), (4) $\text{CH}_3\text{CH}_2\text{COOH}$ (6.3 %), (5) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (1.7 %) (6) Phase II, (7) HCOOH (63.7 %), (8) CH_3COOH (44.3 %), (9) $\text{CH}_3\text{CH}_2\text{COOH}$ (32.7 %), (10) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (34.7 %)

of the 2E3A molecule (*all-trans*-conformation and deprotonated phosphate group), formed a $\text{NH}_3^+ \cdots \text{O-P}$ bond¹⁸ at both ends of 2E3A molecule (Fig. 2(b)), which induced a downfield shift to -15.7 ppm of the single peak (-18.7 ppm for $\alpha\text{-ZrP}$).¹³ Upon adsorption of the carboxylic acids, this downfield shift was not observed, and the signal reappeared at -18 ppm, which was attributable to the reprotonation of the phosphate group by the co-intercalated carboxylic acid molecule^{19-23,25}. Therefore, the adsorption of gaseous carboxylic acid by Phase II resulted in the insertion of the carboxylic acid molecule between the terminal amino group and the layered phosphate, with the reprotonation of the PO_4 group.

Solid-state NMR and XRD data strongly indicate that the adsorption of gaseous carboxylic acids, except for formic acid, by Phase II results the insertion of the carboxylic acid molecule between the terminal amino group and the phosphate layer. Schematic models for the adsorptions are shown in Fig. 8.

FIGURE 8 Schematic model of carboxylic acid adsorption in Phase II

Quaternary ammonium ions cannot be intercalated into layered phosphates, due to the weak electrostatic force and steric hinderance around the active site of the cation. In such a case, the use of alkylamine intercalation compounds has been proposed as means for the intercalation of other guest compounds, which are not directly intercalated. Practically, the intercalation of enzymes with large molecular weights was achieved by using this method²⁶. This method is sometimes called pillar method.

Methylene blue (MB) is a typical thiazine dye, and is well used as a strain in bacteriology, an oxidation-reduction indicator, and disinfectant. Hence, the intercalation of methylene blue into layered phosphate may lead to new functional materials with antibacterial action and good stability. However, it was impossible to intercalate methylene blue in $\alpha\text{-ZrP}$ directly. Therefore, pillar method using butylamine (BA) as pillar, was applied to it, and MB intercalation compound was obtained successfully.²⁵ Therefore, the mechanism of intercalation using pillar was examined precisely.

Figure 9 shows XRD patterns of BA intercalation compound of $\alpha\text{-ZrP}$. On increasing the concentration of BA, several phases with different interlayer distances were observed. The peaks at $d = 1.04$ nm and $1.64\text{--}1.80$ nm are due to the BA intercalation compounds in which BA forms a monolayer and bilayers in the interlayer region, respectively.²¹ XRD patterns of MB-BA cointercalation compounds show new phase with $d = 1.30$ nm is observed around $0.8\text{--}2.0$ mmol of BA addition. This peak will be due to MB intercalation

FIGURE 9 XRD patterns of (a) BA intercalation compound of α -ZrP and (b) MB-BA cointercalation compounds of α -ZrP. Concentration of BA added is shown in the unit of mmol.

compound. This was confirmed by elemental analysis and ^{13}C CP/MAS NMR spectra as shown in Fig. 10. In addition to the peaks due to the CH_3 - and $-\text{CH}_2$ - groups between 10 and 40 ppm, extra peaks due to MB appeared between 100 and 150 ppm. The intensities of these extra peaks were constant at 0.8, 2.0 and 4.0 mmol of BA, and decreased drastically at 6.0 mmol. These results suggest that the intercalation of MB is accelerated by using the BA intercalation compound as a host, but is inhibited by containing too much BA.

The reason for this is closely correlated with the state of BA in the interlayer space. The chemical shift values of BA depend on the amount of BA added. According to the solution NMR data, the ^{13}C chemical shift values of alkylamines vary along with the protonation of amino group, that is, pH of aqueous solution²⁷. Comparing with solution NMR data, at higher concentration (> 2.0 mmol) of BA, $\delta(^{13}\text{C})$ values of α (40.6 ppm), β (29.9 ppm), γ (20.3 ppm), and δ (14.3 ppm) carbons correspond to protonated BA. Therefore, the formation of $-\text{P}-\text{O}\cdots\text{H}_3\text{N}^+$ bond between amine and phosphate is accomplished in bilayer arrangement of BA in the interlayer space, as mentioned in section 3. At a lower concentration (< 2.0 mmol) of BA, $\delta(^{13}\text{C})$ values of α (42.1 ppm), β (36.2 ppm), γ (21.1 ppm), and δ (14.8 ppm) carbons correspond to non-protonated BA. Therefore, there is weak interaction between amino group and phosphate of

host layer. This binding state between amine and phosphate can be confirmed by ^{31}P MAS NMR spectra as well^{20,21}. These results indicated that the intercalation of MB into BA intercalation compound could be achieved by removing BA from the interlayer region in the phase in which BA forms a monolayer (< 2.0 mmol). This is because of weak interaction between amino group and phosphate in monolayer arrangement.

We could successfully clarified full image of the intercalation compound of layered phosphate, that is, structure of layered phosphate, microscopic picture of intercalation compound of layered phosphate, and the correlation between the intercalation compound of layered phosphate and its function. This method was successfully applied to the other intercalation compounds. These works were accomplished mainly by Dr. A. Hayashi, and Dr. M. Danjo.

FIGURE 10 ^{13}C CP/MAS NMR spectra of (1) BA intercalation compound of α -ZrP and (2) BA-MB co-intercalation compound of α -ZrP.

REFERENCES

1. A. Clearfield, J. A. Stynes, *J. Inorg. Nucl. Chem.*, **26**, 117 (1964).
2. A. Clearfield, R. H. Blessing, J. A. Stynes, *J. Inorg. Nucl. Chem.*, **30**, 2249 (1968).
3. C. Y. Ortiz-avila, A. Clearfield, *Inorg. Chem.*, **24**, 1773 (1985).
4. S. Yamanaka, *Inorg. Chem.*, **11**, 2811 (1976).
5. U. Costantino, 1982, *Inorganic Ion Exchange Materials*, A. Clearfield (ed.), CRC Press, Boca Raton.
6. G. Alberti, U. Costantino, 1982, *Intercalation Chemistry*, M. S. Whittingham, A. J. Jacobson (eds.), Academic Press, New York.
7. A. Clearfield, 1994, *Progress in Intercalation Research*, W. Muller-Warmuth and R. Schollhorn (eds.), Kluwer Academic Publ. Dordrecht.

8. A. Clearfield, U. Costantino, 1996, *Comprehensive Supramolecular Chemistry*, Vol. 7, T. Bein and G. Alberti (eds.), Pergamon Press, New York.
9. A. Clearfield, G. D. Smith, , *Inorg. Chem.*, **8**, 431 (1969).
10. J. M. Troup, A. Clearfield, *Inorg. Chem.*, **16**, 3311 (1977).
11. J. Albertsson, A. Oskarsson, R. Tellgren, J. O. Thomas, *J. Phys. Chem.*, **81**, 1574 (1977).
12. D. M. Poojary, B. Shpeizer, A. Clearfield, *J. Chem. Soc. Dalton. Trans.*, **1995**, 111.
13. N. J. Clayden, *J. Chem. Soc. Dalton Trans.*, 1877 (1987).
14. H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, M. Danjo, M. Tsuhako, *J. Mater. Chem.*, **7**, 1063 (1997).
15. A. N. Christensen, I. G. K. Andersen, E. K. Andersen, G. Alberti, M. Nielsen, M. S. Lehmann, *Acta Chem. Scand*, **44**, 865 (1990).
16. M. A. Salvado, P. Pertierra, S. Garcia-Granda, J. R. Garcia, J. Rodriguez, M. T. Fernandez-Diaz, *Acta Cryst.*, **B52**, 896 (1996).
17. M. Tsuhako, M. Danjo, Y. Baba, M. Murakami, H. Nariai, I. Motooka, *Bull. Chem. Soc. Jpn.*, **70**, 143 (1997).
18. A. Hayashi, H. Nakayama, M. Tsuhako, T. Eguchi, N. Nakamura, *Mol. Cryst. Liq. Cryst.*, **341**, 573 (2000).
19. H. Nakayama, A. Hayashi, T. Eguchi, N. Nakamura, M. Tsuhako, *J. Mater. Chem.*, **12**, 3093 (2002).
20. D. J. MacLachlan, K. R. Morgan, *J. Phys. Chem.*, **94**, 7656 (1990).
21. D. J. MacLachlan, K. R. Morgan, *J. Phys. Chem.*, **96**, 3458 (1992).
22. A. Hayashi, H. Nakayama, M. Tsuhako, T. Eguchi, N. Nakamura, *J. Inclusion Phenom.* **34**, 401 (1999).
23. H. Nakayama, M. Danjo, M. Tsuhako, T. Eguchi, N. Nakamura, *Phosphorus Res. Bull.*, **9**, 55 (1999).
24. M. Danjo, A. Hayashi, H. Nakayama, Y. Kimira, T. Shimizu, Y. Mizuguchi, Y. Yagita, M. Tsuhako, H. Nariai, I. Motooka, *Bull. Chem. Soc. Jpn.*, **72**, 2079 (1999).
25. M. Danjo, M. Tsuhako, H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, H. Nariai, I. Motooka, *Bull. Chem. Soc. Jpn.*, **70**, 1053 (1997).
26. Y. Kanzaki, M. Abe, *Bull. Chem. Soc. Jpn.*, **64**, 2292 (1991).
27. J. E. Sarneski, H. L. Surpenant, F. K. Molen, C. N. Reilley, *Anal. Chem.*, **47**, 2116 (1975)