Intercalation of α,ω-Alkanediamines in Layered Aluminium Dihydrogen Triphosphate Dihydrate

AKI HAYASHI, HIROKAZU NAKAYAMA and MITSUTOMO TSUHAKO[*]
Department of Functional Molecular Chemistry, Kobe Pharmaceutical University,
Motoyama-kitamachi, Higashinada-ku, Kobe 658-8558, Japan.

TARO EGUCHI and NOBUO NAKAMURA
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka
560-0043, Japan.

Abstract. Intercalation of α,ω-alkanediamines, $NH_2(CH_2)_nNH_2$ ($n = 3$–10), into layered aluminium dihydrogen triphosphate dihydrate, $AlH_2P_3O_{10}\cdot2H_2O$, was investigated by XRD, DTA-TG, elemental analysis, and solid-state ^{31}P, ^{13}C and ^{27}Al NMR. α,ω-Alkanediamines are intercalated to form a monomolecular layer in the interlayer region, in which the alkanediamines incline at $57 \pm 5°$ to the phosphate layers, whereas n-alkylamines form a bilayer structure with the same inclination angle. Two amino groups in an α,ω-alkanediamine molecule bridge the layered sheets of phosphates.

Key words: intercalation, α,ω-alkanediamine, aluminium dihydrogen triphosphate dihydrate, solid-state NMR.

1. Introduction

In the 1960s Clearfield *et al.* synthesized crystalline layered phosphates of tetravalent metals with large ion-exchange capacities [1, 2]. There are three types of layered phosphates, the α-form (α-M(HPO$_4$)$_2\cdot$H$_2$O, M = Zr, Ti, Hf, Pb, Sn), the γ-form (γ-M(PO$_4$)(H$_2$PO$_4$)$\cdot$2H$_2$O), and AlH$_2$P$_3$O$_{10}\cdot$2H$_2$O (abbreviated as AlP). Extensive work on the intercalation of various organic bases, such as alkylamines and aromatic amines, has been performed on these layered phosphates [3–8]. In the case of α,ω-alkanediamines, full intercalation compounds, Zr(HPO$_4$)$_2\cdot$NH$_2$(CH$_2$)$_n$NH$_2$ ($n = 2, 4, 6, 8, 10$), which have a monomolecular layer, have been reported [9]. The intercalation reaction occurs according to the 'moving boundary model'. α,ω-Alkanediamine, NH$_2$(CH$_2$)$_n$NH$_2$ ($n = 2$–9), intercalation compounds of Ti(HPO$_4$)$_2\cdot$H$_2$O (α-TiP) also have the same monomolecular layer structure in the interlayer region [10]. Calorimetric observation of the reactions of layered phosphates and α,ω-alkanediamines indicated that two amino groups of α,ω-alkanediamines both participate in the acid-base reaction [10]. However,

---

[*] Author for correspondence

the amounts of intercalated α,ω-alkanediamines decrease with increasing alkylene chain length. The uptake of α,ω-alkanediamine into α-TiP is slightly different from that into α-ZrP. Intercalation into AlP, which has an entirely different layer structure from α-ZrP and α-TiP, has been reported only for alkylamine [3], aniline, and pyridine [11]. These works indicated that in addition to strong base, such as alkylamines, AlP can intercalate a weak base like aniline upon irradiation with ultrasonic waves. Therefore, it is of interest to examine the intercalation of α,ω-alkanediamine into AlP, and to compare it with α-ZrP and α-TiP.

Although the intercalation of layered phosphates has been reported in many papers, the structural aspects of intercalation compounds have been investigated only by XRD. The main object of the present paper is to report the microscopic aspects of the intercalation of α,ω-alkanediamine compounds into AlP, studied by solid-state NMR. AlP has been selected as the host compound because microscopic structural information of the host can be obtained from the ^{27}Al nucleus in addition to ^{31}P and ^{13}C nuclei.

In this report, α,ω-alkanediamine intercalation compounds of AlP were synthesized and characterized by XRD, DTA-TG, elemental analysis, and solid-state ^{31}P, ^{13}C and ^{27}Al NMR. For comparison, the alkylamine intercalation compounds of AlP were also investigated.

2. Experimental

2.1. PREPARATION

Layered aluminium dihydrogen triphosphate dihydrate, $AlH_2P_3O_{10}\cdot 2H_2O$ (AlP), was prepared according to the reported procedure [12]. The AlP obtained was identified by elemental analysis and X-ray diffractometry.

n-Alkylamines, $CH_3(CH_2)_{x-1}NH_2$ ($x = 1, 2, 3, 4, 5$), and α,ω-alkanediamines, $NH_2(CH_2)_nNH_2$ ($n = 2, 3, 4, 6, 7, 8, 9, 10$), were guaranteed reagents from Wako Chemical Industries Ltd. 1,5-Pentanediamine and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) were purchased from Aldrich Chem. Co., and Sigma, respectively. They were used without further purification. In order to discover the optimum conditions for the intercalation of α,ω-alkanediamines, the concentration and the reaction time dependence of uptakes were measured for 1,4-butanediamine and 1,10-decanediamine. It was found that the intercalation compounds could be obtained by suspending AlP (3.0 g) in 0.1 dm^3 of 0.1 mol dm^{-3} α,ω-alkanediamine aqueous solution and stirring at room temperature for 5 h. The other α,ω-alkanediamine intercalation compounds were also prepared under the same conditions. However, no 1,2-ethanediamine intercalation compound of AlP could be obtained at all under conditions of 25–80 °C, 5 h–1 day, and 0.03–0.2 mol dm^{-3} 1,2-ethanediamine.

For the intercalation of alkylamines, AlP (3.0 g) was suspended in 0.1 dm^3 of 0.1 mol dm^{-3} alkylamine aqueous solution in an Erlenmeyer flask and the suspen-

sion was stirred at room temperature for 5 h. The resultant products were filtered, washed with distilled water, and then dried in air at room temperature.

2.2. ANALYTICAL PROCEDURES

Powder X-ray diffraction patterns were measured using a Rigaku Denki Rint 2000 diffractometer using Ni-filtered CuK_α radiation to monitor all new phases and to measure their interlayer distances. The α,ω-alkanediamine and water contents in the intercalation compounds were determined by elemental analysis and DTA-TG using a Sumigraph NC-90A and Rigaku Denki Differential Thermogravimetric Analyzer (TG8110), respectively.

The solid-state NMR spectra of host AlP and the intercalation compounds were obtained by a Bruker DSX-200 spectrometer operating at 81.0, 50.3, and 52.15 MHz for ^{31}P, ^{13}C, and ^{27}Al nuclei, respectively. A single-pulse sequence with a $\pi/2$ pulse of 2 μs, a recycle delay of 20 s, and accumulation of 8 FID signals was used to obtain ^{31}P MAS (Magic Angle Spinning) NMR spectra with ^{1}H high-power decoupling. ^{13}C CP/MAS NMR spectra were measured using a recycle time of 4 s and an accumulation of up to 9600 scans. ^{27}Al MAS and Static NMR spectra with ^{1}H high-power decoupling were acquired using a 2 s recycle delay and 640 accumulations. MAS rates for all the measurements were 3–4 kHz. The chemical shift references of ^{31}P, ^{13}C, and ^{27}Al nuclei were 85% H_3PO_4 aqueous solution, TMS, and 1 mol dm^{-3} $AlCl_3$ aqueous solution, respectively. ^{13}C FT NMR spectra of alkylamine and α,ω-alkanediamine aqueous solutions were obtained with a Varian Gemini-300 spectrometer.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of α,ω-alkanediamine intercalation compounds of AlP. On intercalating α,ω-alkanediamines into AlP the diffraction peak of the host AlP ($d = 7.95$ Å) disappeared completely and new peaks appeared at lower angle, except for the case of 1,2-ethanediamine, indicating that α,ω-alkanediamines were intercalated into AlP to expand the interlayer distance. The elemental analyses of all the intercalation compounds showed that about one mole of α,ω-alkanediamine per one mole of $AlH_2P_3O_{10}\cdot 2H_2O$ is intercalated. And the results of DTA-TG showed that two moles of water per mole of $AlH_2P_3O_{10}\cdot 2H_2O$ exist in the intercalation compound. Therefore, half of the maximum intercalation capacity of AlP (6.87 mmol per 1 g of AlP) is occupied by α,ω-alkanediamine. This means that almost all the hydrogen phosphate sites (P—OH) in AlP reacted with two amino groups of α,ω-alkanediamine. However, 1,2-ethanediamine was not intercalated into AlP, in contrast to α-ZrP and α-TiP, although it needed a longer reaction time (30 days) and high temperature (80 °C) to obtain the 1,2-ethanediamine intercalation compound of α-ZrP [9]. In spite of our efforts to achieve the reaction under various conditions (25–80 °C, 5 h–1 day, 0.03–0.2
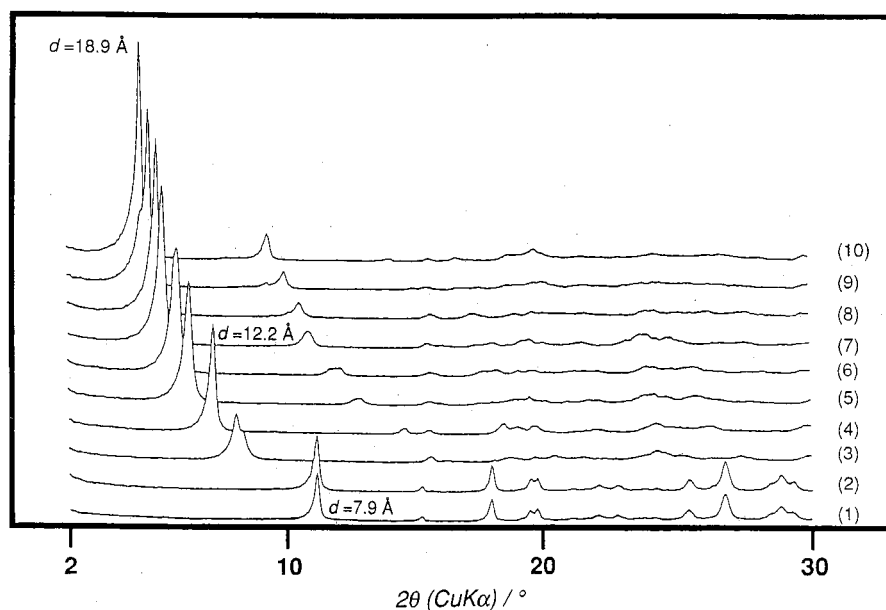
Figure 1. X-ray diffraction patterns of (1) AlP and the intercalation compounds of (2) 1,2-ethanediamine, (3) 1,3-propanediamine, (4) 1,4-butanediamine, (5) 1,5-pentanediamine, (6) 1,6-hexanediamine, (7) 1,7-heptanediamine, (8) 1,8-octanediamine, (9) 1,9-nonane-diamine, and (10) 1,10-decanediamine, respectively.

mol dm^{-3}), the 1,2-ethanediamine intercalation compound of AlP could not be obtained. The reason why 1,2-ethanediamine is not intercalated into AlP will be discussed later.

On increasing the number of carbon atoms (n) in the α,ω-alkanediamine the interlayer distance (d) increases linearly (Figure 2), suggesting that intercalated α,ω-alkanediamines are regularly oriented in the interlayer region of AlP and the angle to the phosphate layer is constant. This linear correlation has been used to estimate the inclination of guest molecule to the layer as well as its arrangement with either a mono- or a bilayer structure [3, 6, 9, 10, 13]. The slope of the straight line is calculated to be 1.07 ± 0.06 Å/atom, suggesting that α,ω-alkanediamines incline at an angle of $57 \pm 5°$ to the plane of the layered AlP and form a monolayer structure with all-*trans* conformation in the interlayer region. The extrapolated in-terlayer distance for $n = 0$ coincides with 7.95 Å of the host AlP itself, supporting the above model arrangement. This inclination angle is almost the same as those of α,ω-alkanediamine intercalation compounds of α-ZrP and α-TiP [9, 10] and those of alkylamine intercalation compounds of layered phosphates [3, 13]. As shown in Figure 2, the interlayer distances of alkylamine intercalation compounds agree with those of α,ω-alkanediamine intercalation compounds, if the number of carbon atoms in the alkylamine is counted double. It is thus obvious that alkylamine forms
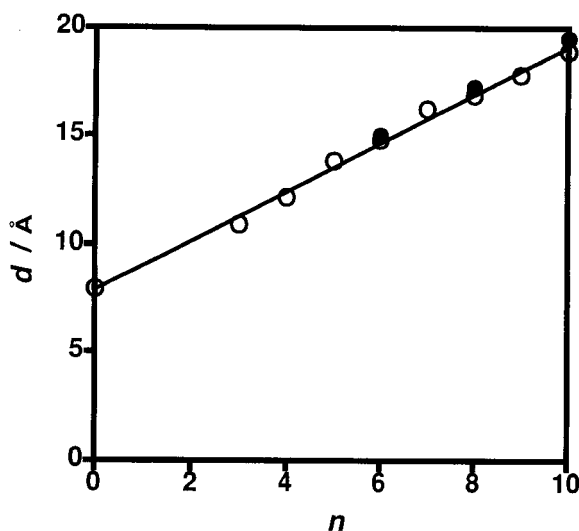
Figure 2. Interlayer distances (*d*) of the α,ω-alkanediamine (○) and alkylamine (●) intercalation compounds of AlP as a function of the number of carbon atoms (*n*) in the alkylene chain. In the case of alkylamine, the number of carbon atoms is counted double, assuming a bilayer structure.

a bimolecular structure in the interlayer region of AlP and the inclinations of both alkylamine and α,ω-alkanediamine molecules are almost the same.

The solid-state ^{31}P, ^{13}C, and ^{27}Al NMR spectra were measured to reveal the microscopic interaction between the host AlP and α,ω-alkanediamines. Figure 3 shows the solid-state ^{31}P MAS NMR spectra of the host AlP with (Figure 3(a)) and without ^{1}H high-power decoupling (Figure 3(b)). Triphosphate ion, $H_2P_3O_{10}^{3-}$, is a condensed phosphate and is composed of two end phosphate groups and one middle phosphate group. Two peaks of the host AlP observed at −21 and −32.5 ppm in the ^{31}P MAS NMR spectrum (Figure 3(b)) are attributable to the end and middle phosphate groups, respectively, by considering the intensity ratio of the two peaks and solution NMR data [14]. However, it is not easy to assign these two peaks definitely because the crystal structure of AlP has not yet been resolved. As demonstrated in the previous paper [15], it is possible to distinguish different phosphate groups, PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$, by comparing ^{31}P MAS NMR spectra with and without ^{1}H high-power decoupling, and also by ^{31}P CP/MAS NMR spectra, since [31]P-^{1}H dipolar interactions in these phosphate groups vary by several orders of magnitude. The broad signal due to the dipolar interaction of hydrogen atoms can be removed by applying ^{1}H high-power decoupling measurement. Compared with the spectra with and without ^{1}H high-power decoupling of AlP (Figure 3), a peak at −32.5 ppm does not change on decoupling, while a peak at −21 ppm becomes sharper and splits into a doublet with equal intensity. This result indicates that the peaks at −20.8 and −22.8 ppm are due to the end phosphate groups and that two hydrogen atoms of the $H_2P_3O_{10}^{3-}$ group are bonded to the end phosphate

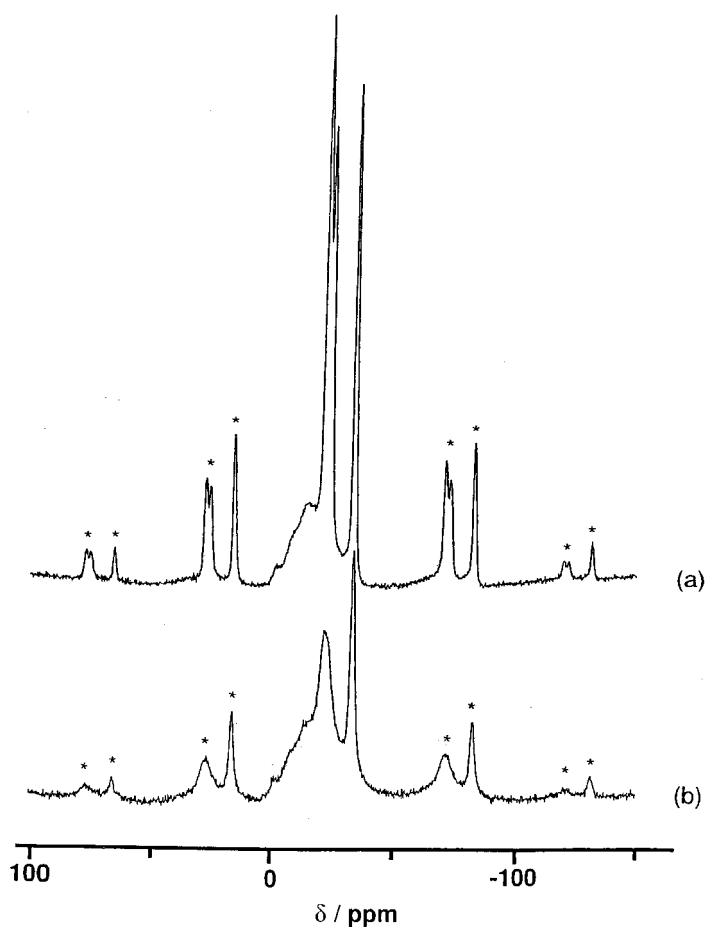*Figure 3.* ^{31}P MAS NMR spectra of $AlH_2P_3O_{10} \cdot 2H_2O$, (a) with ^{1}H high-power decoupling and (b) without ^{1}H high-power decoupling. A broad peak at -14 ppm is due to impurities of AlP itself. * shows spinning side bands.

groups. Further, the peak at -32.5 ppm is due to the middle phosphate group. This is consistent with the preliminary assignment by solution NMR data [14]. The fact that the peak of the end phosphate groups splits into a doublet indicates that the AlP molecule contains two crystallographically non-equivalent end phosphate groups, although the two end phosphate groups are equivalent in solution [14].

Figure 4 shows the ^{31}P MAS NMR spectra of α,ω-alkanediamine and alkylamine intercalation compounds of AlP. For α,ω-alkanediamine intercalation compounds (Figure 4) two peaks are mainly observed at around -17 and -28 ppm, regardless of the length of the alkylene chain. No peak of the host AlP is observed in Figure 4, indicating that the intercalation is complete, and that the arrangements of the α,ω-alkanediamines in the interlayer region are almost the same regardless of the alkylene chain length, consistent with the results of XRD and elemental
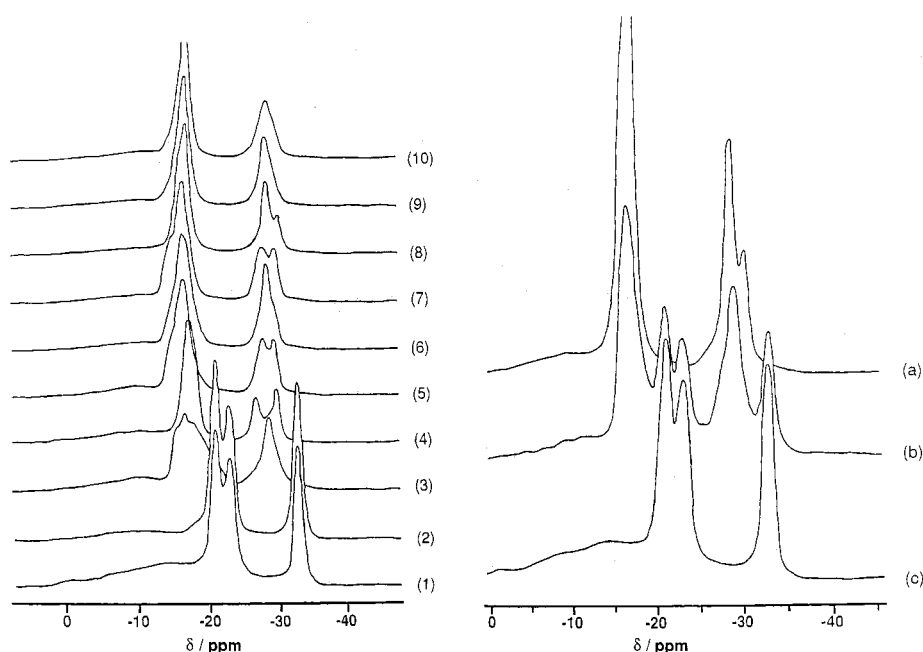
Figure 4. ^{31}P MAS NMR spectra with ^{1}H high-power decoupling of (1), (c) AlP and the intercalation compounds of (2) 1,2-ethanediamine, (3) 1,3-propanediamine, (4) 1,4-butanediamine, (5) 1,5-pentanediamine, (6) 1,6-hexanediamine, (7) 1,7-heptanediamine, (8) 1,8-octanediamine, (9) 1,9-nonanediamine, (10) 1,10-decanediamine, and (a) 1,8-octanediamine, (b) butylamine.

analysis. By performing the same experiment as the assignment of the spectra of host AlP [15], the peaks of the intercalation compounds at around −17 and −28 ppm could be assigned to the end and the middle phosphate groups, respectively. Two possible mechanisms of the large lower field shift are as follows.

(1) It is well known that the peaks of the alkylamine intercalation compounds of α-ZrP shift by +3.7 ppm from that of α-ZrP (−18.7 ppm) in ^{31}P MAS NMR spectra because of the deprotonation of the phosphate group (—P—OH → —P—O$^-$ ⋯ H$_3$N$^+$—) [16].

(2) The interaction between the phosphate group and the water molecule may induce this shift. In α,ω-alkanediamine intercalation compounds two water molecules remain per one AlH$_2$P$_3$O$_{10}$.

It is hard to determine the position of the water molecules in the intercalation compounds, because single-crystal X-ray structural analysis of intercalation compounds is difficult. However, Morgan *et al.* reported that the ^{31}P MAS NMR signal of the *n*-propylamine intercalation compound of α-ZrP shifts less than 1.2 ppm on dehydration [16]. This is because the strong interaction between the phosphate group and the amino group of *n*-propylamine excludes the interaction between the

phosphate group and the water molecule. The situation will be similar in the α, ω-alkanediamine intercalation compounds of AlP. Therefore, by mechanism (1), two peaks (-20.8 and -22.8 ppm) of the end phosphate groups in AlP are considered to shift to -16.5 ppm by intercalation. That is, the end phosphate groups deprotonate to form the —P—O$^-$ $\cdots$ H$_3$N$^+$— bond on intercalating α,ω-alkanediamines. The peak at -32.5 ppm due to the middle phosphate group also shifts to a lower field by $+4$ ppm, indicating the existence of a weak hydrogen bond between the α,ω-alkanediamine and the middle phosphate group. On closely examining the line shape of the middle phosphate group, the shape is found to depend on the alkylene chain length. For example, two peaks with a splitting of 3 ppm are observed for 1,4-butanediamine. However, the separation between the two peaks reduces with increasing alkylene chain length. There is no splitting for 1,10-decanediamine. As will be discussed later, the splitting of the peak at around -28 ppm might be related to the deformation of the host AlP.

The alkylamine intercalation compounds of AlP showed similar spectra to the α,ω-alkanediamine intercalation compounds, although the peak of unreacted host AlP remained, as expected from the X-ray diffraction pattern. The chemical shift value of the alkylamine intercalation compound (Figure 4b) with a bilayer structure is almost the same as that of the α,ω-alkanediamine intercalation compound with a monolayer structure (Figure 4b), suggesting that the local bond scheme of —P—O$^-$ $\cdots$ H$_3$N$^+$— in the alkylamine intercalation compound is similar to that of α,ω-alkanediamine in the interlayer region.

The formation of a —P—O$^-$ $\cdots$ H$_3$N$^+$— bond in α,ω-alkanediamine and alkylamine intercalation compounds was also confirmed by ^{13}C CP/MAS NMR spectra. Table I summarizes the chemical shift values of ^{13}C NMR spectra of the 1,4-butanediamine and butylamine intercalation compounds, and those of guest compounds in aqueous solution [17]. When 1,4-butanediamine is protonated in an aqueous acid solution (specified as acid in Table I), the β-carbon shows an upfield shift. By comparing the chemical shift values of the β-carbons, α,ω-alkanediamine and alkylamine in the interlayer region were concluded to be protonated. Both ^{31}P and ^{13}C NMR spectra suggest the formation of a —P—O$^-$ $\cdots$ H$_3$N$^+$— bond in the α,ω-alkanediamine and alkylamine intercalation compounds.

Because the ^{31}P NMR signal of the end phosphate groups appears only at -17 ppm and no peak appears at -21 ppm (host AlP), no protonated phosphate remains. The ^{13}C NMR chemical shift values of the two β-carbons suggest the protonation of the two amino groups in α,ω-alkanediamine. Furthermore, the elemental analysis shows that one α,ω-alkanediamine is intercalated per two end phosphate groups. These experimental results strongly suggest that the two amino groups of a α,ω-alkanediamine are protonated by the protons of two end phosphate groups to connect two layers of phosphates. Airoldi *et al.* demonstrated the formation of a —P—O$^-$ $\cdots$ H$_3$N$^+$— bond from the measurement of the standard enthalpy of the intercalation of α,ω-alkanediamines into α-TiP [10]. This bridging model – that

Table I. ^{13}C NMR chemical shift data of amines in aqueous solution and intercalated in AlP.

Amine and diamine	δ/ppm			
	C_α	C_β	C_γ	C_δ
NC₄N⟨base[a]	43.6	32.4	–	–
acid[b]	41.5	26.4	–	–
NC₄N in AlP	40.5, 39.8	26.0, 24.8	–	–
C₄N⟨base[a]	43.5	37.7	22.5	16.2
acid[b]	42.0	31.2	21.6	15.6
C₄N in AlP	39.6	30.6, 29.8	20.3	14.1

[a] 1.0 g amines in 1.0 ml D_2O.
[b] One equivalent molars of DCl added.

is, the two amino groups of a α,ω-alkanediamine connect two phosphate layers – indirectly supports the all-*trans* conformation of an α,ω-alkanediamine in the interlayer region deduced from XRD data.

Although the crystal structure of AlP is wholly different from those of α-ZrP and α-TiP, the arrangement of α,ω-alkanediamines and the formation of a —P—O⁻ ···H₃N⁺— bond in the interlayer region are the same. However, there are some minor differences between the intercalation compounds of AlP and α-TiP. The amount of α,ω-alkanediamine intercalated in α-TiP decreased on increasing the alkylene chain length, although our data on AlP showed that α,ω-alkanediamines are completely intercalated, regardless of the alkylene chain length, similar to the case of α-ZrP. At present it is hard to understand the difference. No 1,2-ethanediamine intercalation compound of AlP could be obtained at all, in contrast to the fact that 1,2-ethanediamine intercalation compounds of α-ZrP and α-TiP have been reported. The difficulty of 1,2-ethanediamine intercalation in layered phosphate is partly understood by reference to the ^{27}Al NMR spectra presented below.

Figure 5 shows the ^{27}Al MAS NMR spectra of 1,8-octanediamine and butylamine intercalation compounds, together with that of host AlP itself. The spectra of the other α,ω-alkanediamine and alkylamine intercalation compounds showed almost the same patterns. The asymmetric line shape of AlP is due to the quadrupole interaction. Simulation by using the parameters, $\delta_{iso} = -20$ ppm, $e^2Qq/h = 351$ kHz, $\eta = 0$, can reproduce this powder pattern well [18]. The isotropic chemical shift value suggests that Al is octahedrally coordinated with the oxygen atoms of phosphate groups [19]. The octahedron is slightly deformed, as evidenced by e^2Qq/h. In the spectrum of an alkylamine intercalation compound, the spectra are composed of those of the alkylamine intercalation compound and host AlP. From the results of elemental analysis and ^{31}P NMR spectra, the ratio of these two components is roughly 2 : 1. Therefore, the sharp component with a line width of
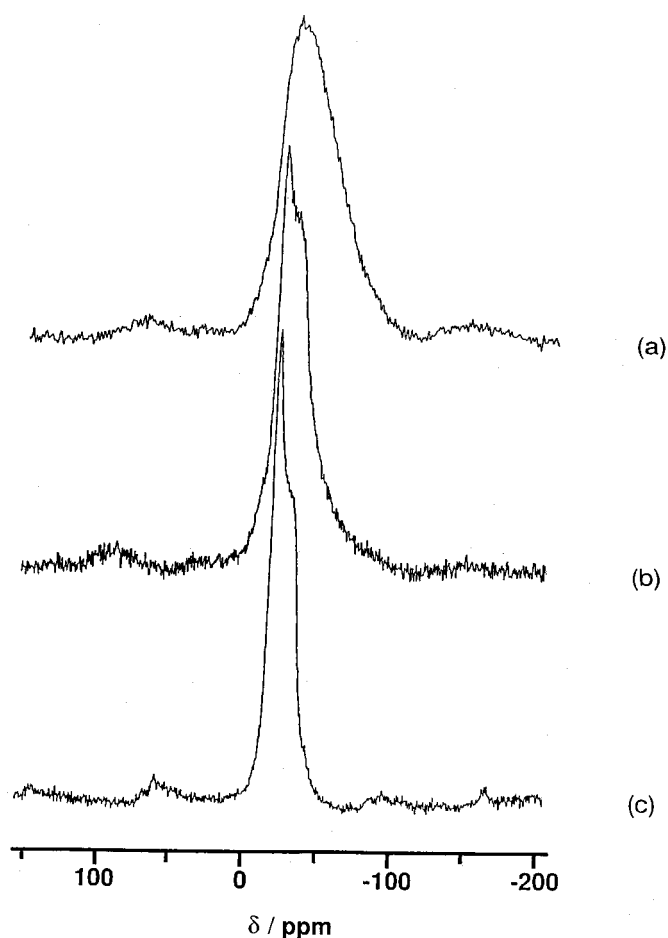
Figure 5. ^{27}Al MAS NMR spectra with ^{1}H high-power decoupling of (a) 1,8-octanediamine, (b) butylamine intercalated in AlP, and (c) AlP.

50 ppm is due to the alkylamine intercalation compound and also to host AlP. The spectra of alkylamine intercalation compounds are almost similar to that of the host AlP. By contrast, the spectra of α,ω-alkanediamine intercalation compounds are broadened appreciably compared with those of AlP and alkylamine intercalation compounds. In general, a sharp spectrum is observed for the octahedrally coordinated ^{27}Al atom [18]. Therefore, the broad spectra of α,ω-alkanediamine intercalation compounds suggest that octahedral coordination of Al atom is deformed considerably in comparison with that in the host AlP and the alkylamine intercalation compounds. This is probably due to the fact that the α,ω-alkanediamine molecule bridges two layers of the host AlP. The deformation is also reflected in the ^{31}P MAS NMR spectra of α,ω-alkanediamine intercalation compounds. As mentioned above, a peak of the middle phosphate group in ^{31}P MAS NMR spectra
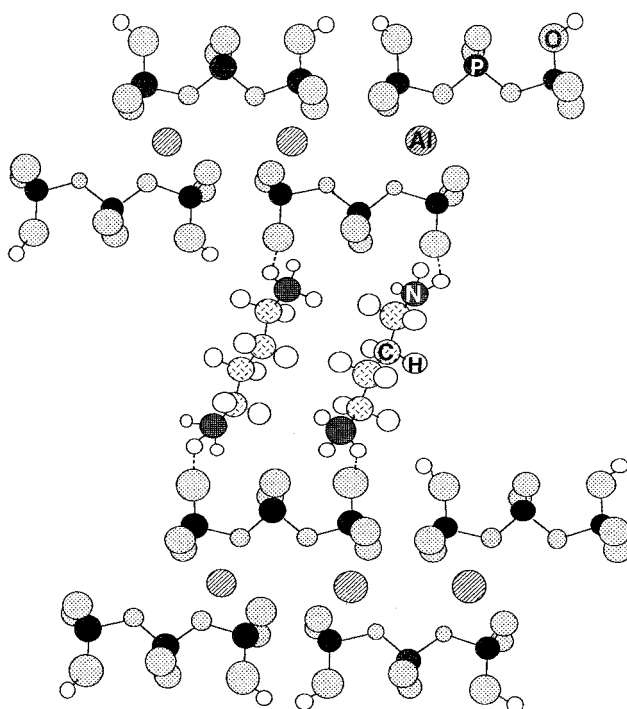
Figure 6. Schematic structural model of the 1,4-butanediamine intercalation compound of AlP.

splits into a doublet. The separation of the doublet decreased with increasing alkylene chain length. This phenomenon is explained as follows. The layer of the host molecule is largely deformed by the bridging due to the α,ω-alkanediamine with a short alkylene chain such as 1,4-butanediamine, whereas this strain is gradually reduced with increasing alkylene chain length. This strain model might also explain the fact that the 1,3-propanediamine intercalation compound of AlP shows broad XRD and NMR patterns, and that no 1,2-ethanediamine intercalation compound could be obtained at all for AlP. For the same reason, the 1,2-ethanediamine intercalation compounds of α-ZrP [9] and α-TiP [10] have been prepared under limited conditions (80 °C, 30 days).

In spite of the large strain of the layer in α,ω-alkanediamine intercalation compounds, α,ω-alkanediamine (n = 3–10) could be perfectly intercalated into AlP. This is probably due to the large exothermic enthalpy (−56 kJ/mol) resulting from the strong interaction of the phosphate group (P—OH) with two amino groups [10].

Figure 6 represents a proposed structural model of the 1,4-butanediamine intercalation compound of AlP. An aluminium atom exists between triphosphates and is octahedrally coordinated with oxygen atoms of the phosphates. α,ω-Alkanediamine is protonated by receiving hydrogen atoms of the end phosphate groups and is intercalated with an inclination angle of 57 ± 5° to the phos-

phate layer. The other hydrogens of the amino groups form a weak hydrogen bond with the oxygen atom of the middle phosphate group. The AlO_6 octahedron is considerably deformed by bridging two layers of the host molecule with α,ω-alkanediamine.

In conclusion, the formation of an α,ω-alkanediamine intercalation compound of AlP with the $—P—O^-\cdots H_3N^+—$ bond in the interlayer region can be microscopically evidenced by ^{31}P and ^{13}C solid-state NMR. Although α,ω-alkanediamines ($n = 2–10$) are intercalated into α-ZrP and α-TiP, 1,2-ethanediamine could not be intercalated into AlP. From the results of ^{27}Al and ^{31}P NMR spectra, it is found that α,ω-alkanediamine bridges two layers of AlP to deform the layer structure of host AlP.

References

1. A. Clearfield and J. A. Stynes: *J. Inorg. Nucl. Chem.* **26**, 117 (1964).
2. A. Clearfield, R. H. Blessing, and J. A. Stynes: *J. Inorg. Nucl. Chem.* **30**, 2249 (1968).
3. M. Tsuhako, K. Kawamoto, M. Danjo, Y. Baba, M. Murakami, H. Nariai, and I. Motooka: *Nippon Kagaku Kaishi* 944 (1992).
4. G. Alberti and U. Costantino: *Intercalation Chemistry*, ed by M. S. Whittingham and A. J. Jacobson, Academic Press, New York, 1982.
5. M. Danjo, Y. Baba, M. Tsuhako, H. Nariai, and I. Motooka: *Phosphorus Res. Bull.* **3**, 25 (1993).
6. M. Danjo, Y. Baba, M. Tsuhako, S. Yamaguchi, M. Hayama, H. Nariai, and I. Motooka: *Bull. Chem. Soc. Jpn.* **68**, 1607 (1995).
7. L. Szirtes, J. Kornyei, and Z. Poko: *Reactive Polymers* **7**, 185 (1988).
8. U. Costantino: *Inorganic Ion Exchange Materials*, ed. A. Clearfield, CRC Press, Boca Raton, FL, 1982; A. Clearfield: *Progress in Intercalation Research*, ed. W. Muller-Warmuth and R. Schollhorn, Kluwer Academic, Dordrecht, 1994; A. Clearfield and U. Costantino: *Comprehensive Supermolecular Chemistry*, ed. T. Bein and G. Alberti, Pergamon Press, NY, Vol. 7 (1996).
9. M. Casciola, U. Costantino, L. D. Croce, and F. Marmottini: *J. Incl. Phenom.* **6**, 291 (1988).
10. C. Airoldi and S. Roca: *J. Mater. Chem.* **6**, 1963 (1996).
11. H. Tagaya, S. Sato, N. Kuramoto, J. Kadokawa, M. Karasu, and K. Chiba: *J. Incl. Phenom.* **18**, 193 (1994).
12. M. Tsuhako, K. Hasegawa, T. Matsuo, I. Motooka, and M. Kobayashi: *Bull. Chem. Soc. Jpn.* **48**, 1830 (1975).
13. F. Menendez, A. Espina, C. Trobajo, J. R. Garaca, and J. Rodriguez: *J. Incl. Phenom.* **15**, 215 (1993); Y. Kanzaki, and M. Abe: *Bull. Chem. Soc. Jpn.* **64**, 1846 (1991).
14. Bv John R. Van Wazer, Clayton F. Callis, James N. Shoolery, and Robert C. Jones: *J. Am. Chem. Soc.* **78**, 5715 (1956).
15. H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, M. Danjo, and M. Tsuhako: *J. Mater. Chem.* **7**, 1063 (1997).
16. M. Danjo, M. Tsuhako, H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, H. Nariai, and I. Motooka: *Bull. Chem. Soc. Jpn.* **70**, 1053 (1997); D. J. Maclachlan and K. R. Morgan: *J. Phys. Chem.* **94**, 7656 (1990).
17. J. E. Sarneski, H. L. Surprenant, F. K. Molen, and C. N. Reilley: *Anal. Chem.* **47**, 2116 (1975).
18. H. J. Behren and B. Schnabel: *Physica* **114B**, 185 (1982).
19. R. J. Kirkpatrick, K. A. Smith, S. Schramm, G. Turner and H. W. Yang: *Ann. Rev. Earth Planet Sci.* **13**, 29 (1985).