

Orientation of an Organic Anion and Second-Staging Structure in Layered Double-Hydroxide Intercalates

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Mg–Al layered double hydroxides (LDHs) intercalated with an anionic azobenzene derivative (AzAA) were prepared, and the arrangement of the incorporated AzAA was investigated by varying the starting AzAA/LDH ratios for two types of LDHs with different Mg/Al mole ratios, Mg/Al = 2.0 (LDH2) and 3.0 (LDH3). The observed basal spacings of the complexes, 8 and 23–25 Å, were ascribed to horizontal (parallel to the layers) and vertical (perpendicular to the layers) orientations of the incorporated AzAA, respectively. In general, the horizontal orientation was observed with low AzAA/LDH ratios and the vertical orientation was observed with higher ratios. For the LDH2 complexes, a large basal spacing of 33 Å was observed with intermediate AzAA/LDH ratios, that is, 0.5 and 0.75, which was interpreted as an alternate stacking of the two types of interlayers (“1:1 ordered interstratification” or “second staging”). In the case of the LDH3 complexes having a smaller layer-charge density, second staging was not found with the intermediate AzAA/LDH ratios; instead, two separated phases, 8 and 23 Å, were obtained. TEM images for the complexes with basal spacings of 33 and 25 Å were consistent with the proposed structure model.

Introduction

Layered inorganic compounds such as clay minerals and layered double hydroxides (LDHs) have been used to prepare nanoscale organic/inorganic layered complexes in efforts to develop new functional materials.¹ In developing these functional materials, it is essential to control the orientation of incorporated organics in the interlayer space to fully utilize the anisotropic properties of the functional organics. In addition to the orientation of the organics in the interlayer space, the mode of the layer stacking is also important in controlling the arrangement of complexes. Layer stacking is related to the phenomenon of “interstratification,” a term used within mineralogy for layered compounds with two or more kinds of layers stacked in either ordered or random ways.^{2,3} While random interstratification is generally observed in clays,² ordered interstratification is common in other layered compound systems such as graphite.^{4,5} In graphite systems, intercalation takes place every few layers and this phenomenon is referred to as “staging,” and when intercalation occurs for every other layer, being equivalent to the 1:1 ordered interstratification, the phenomenon is called “second staging.”⁴ The importance of layer stacking is manifested in the case of a

two-dimensional layered compound, $K_4Nb_6O_{17}$, having two kinds of interlayers arranged in alternate ways, which were assumed to play important roles in its photocatalytic efficiency.⁶

In the present study, the orientation of guest organic molecules and the staging phenomenon were investigated for the organic/LDH complexes. Mg–Al–LDHs were used as the host layered material. LDHs consist of positively charged metal hydroxide layers with anions located at the interlayer space for charge compensation. The general formula for MgAl–LDH is expressed as $Mg_{1-x}Al_x(OH)_2(OH)_x \cdot mH_2O$, where $x = 0.1–0.34$ and $m = 1 - 3x/2$.^{7,8} The complexes were prepared by varying the organics/LDH ratio and the Mg/Al ratio of the host LDHs. The layer charge of LDH can be controlled by changing the cation ratio (Mg/Al).

Although the majority of articles concerned with LDHs and clay minerals have described the orientation of incorporated organic molecules, only a few cases of staging have been reported. The scarcity of these phenomena has been rationalized theoretically in terms of the stiffness of the host planes and interplane attractive forces.⁹ Among the few reported cases,^{10–13} Ijdo and Pinnavaia¹¹ have discussed the factors for obtaining second staging in the intercalation of smec-

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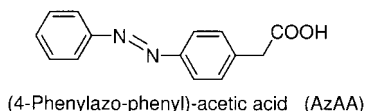


Figure 1. Molecular structure of AzAA.

tites with various alkylammonium ions. Kooli et al.¹² have reported the appearance of second staging for telephthalic acid/MgAl-LDH complexes by heating. The formation of a second-staging intermediate was observed for $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot\text{H}_2\text{O}$ in the intercalation of dicarboxylate anions by time-resolved X-ray diffraction.¹³

In the present paper, the orientation of the guest molecules and staging structure are discussed in terms of the molecular dimensions and the charge density of the host LDHs on the basis of data obtained by CHN analysis, powder X-ray diffraction (PXRD), and transmittance electron microscopy (TEM).

Experimental Section

Materials. The guest azo derivative was (4-phenylazophenyl)acetic acid (AzAA, Figure 1) synthesized as shown in Scheme 1. The details of the synthesis are described in the following subsection. The host material was LDH composed of Al and Mg. The coprecipitation method was employed to produce AzAA-LDH complexes. The reagents used were $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ (reagent grade, Kanto Chemical Co., Ltd.), and 50% NaOH aqueous solution. They were used after being adjusted to the appropriate concentration by degassed deionized water.

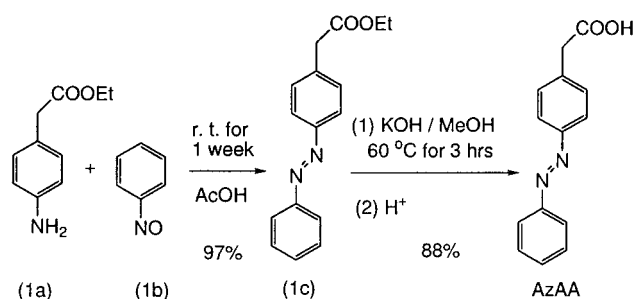
Synthesis of the Azo Derivative. The azobenzene derivative, AzAA, shown in Figure 1 was synthesized as follows.

(4-Phenylazophenyl)acetic Acid Ethyl Ester (1c). **1c** was obtained by coupling (4-aminophenyl)acetic acid ethyl ester (**1a**, 4.5 g, reagent grade, Kanto Chemicals Co., Ltd.) and nitroso benzene (**1b**, 3.73 g, Tokyo Kasei Kogyo Co., Ltd.) in glacial acetic acid at room temperature for 1 week. After water was added, the precipitate was separated by filtering, and the obtained yellow solid was extracted by hot *n*-hexane. The resulting orange solution was filtered and condensed for recrystallization. Orange needles (6.55 g), yield: 97%; M_w 268.31, m.p. 84.5–85 °C. MS (EI): m/z 268 [M^+]. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$: C, 71.62; H, 6.01; N, 10.44 wt %. Found: C, 71.4; H, 6.1; N, 10.4 wt %.

(4-Phenylazophenyl)acetic Acid. Hydrolysis of 5.8 g (**1c**) was conducted by 1 N KOH/methanol by reflux in a nitrogen atmosphere for 2.5 h. After removal of the solvent, the remainder was acidified by hydrochloric acid and extracted by ethyl acetate. Recrystallization was from ethanol. Orange flakes (4.57 g), yield: 88%; M_w 240.26, m.p. 191.5–192.5 °C. MS (EI): m/z 240 [M^+]. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$: C, 69.99; H, 5.03; N, 11.66 wt %. Found: C, 69.9; H, 5.1; N, 11.7 wt %. ^1H NMR (300 MHz, (DMSO- d_6): δ 12.45 (br. s., 1H, COOH), 7.87 (m, 4H, Ar-H), 7.58 (m, 5H, Ar-H), 3.71 (s, 2H, Ar-CH₂-).

Preparation of the Complexes. AzAA/LDH complexes were synthesized by a coprecipitation method similar to that already reported.^{7,14} Two types of LDHs with different Mg/Al ratios (in mol) were employed: one was Mg/Al = 2.0 (LDH2), and the other was Mg/Al = 3.0 (LDH3). The AzAA/LDH ratio was changed from 0 to 2. Here, the mole ratios (AzAA/LDH) are based on the formula $\text{Mg}_2\text{Al}(\text{OH})_6(\text{OH})\cdot 2\text{H}_2\text{O}$ for LDH2 and

Scheme 1



$\text{Mg}_3\text{Al}(\text{OH})_8(\text{OH})\cdot 2\text{H}_2\text{O}$ for LDH3. In other words, the ratios were calculated against Al in the LDH, which corresponds to the amount of exchangeable anion sites in LDH. The general synthetic process was as follows.

Aqueous solutions of MgCl_2 and AlCl_3 ($\text{Mg} + \text{Cl} = 0.5$ mol/L), NaOH (1.125 mol/L for LDH3 and 1.167 mol/L for LDH2), and an aqueous solution of AzAA sodium salt (0.125 mol/L for AzAA/LDH = 1.0), which was prepared from AzAA and NaOH solution, were continuously added to a flask at the same flow rate of about 40 mL/min under vigorous stirring in a nitrogen atmosphere. After the pH of the resultant suspension was adjusted to within 10–11.5, the suspension was divided into three portions and each portion was further treated at room temperature (20–25 °C), 60 °C, and 100 °C (reflux) for 18–20 h in a nitrogen atmosphere, respectively. After these “aging” treatments, the resulting precipitates were filtrated through a membrane filter with a pore size of 0.2 μm (Millipore filter) and thoroughly washed with degassed deionized water several times to remove the nonreacted reagents. The precipitate was dried in a vacuum for 1 night, yielding yellowish orange solids.

Characterization Techniques. For determination of the compositions of the AzAA/LDH complexes, CHN analysis was conducted using a Sumigraph NCH-21 (Sumika Chemical Analysis Service, Co. Ltd.) and a Perkin-Elmer 2400 II CHN element analyzer. The amounts of Mg and Al were analyzed by ICP for the diluted nitric acid solution after a decomposition treatment. The wavelength used for the Mg and Al analyses were 285.213 and 396.152 nm, respectively.

For characterization of the prepared AzAA, ^1H NMR was conducted using a Bruker AC300P (300 MHz) and a JEOL EX270 (200–270 MHz) (Sumika Chemical Analysis Service, Co. Ltd.). Mass spectroscopy (MS(EI)) was conducted using a JEOL AX-505W (Sumika Chemical Analysis Service, Co. Ltd.).

Powder X-ray diffraction of the complexes was conducted at a scanning speed of $2\theta = 2^\circ/\text{min}$ using a RINT 1200 (Rigaku Co. Ltd.) diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm). The measurement was conducted at 18–22 °C in an ambient atmosphere. In the present paper, the reflection indices are based on the *c*-axis length of a hexagonal subcell containing one interlayer space, which is one-third of that of the 3R-polytype hydroxalcalite unit cell.¹⁵ The d_{001} for the subcell corresponds to the d_{003} for the unit cell. A two-dimensional electron density map was also obtained by using a program incorporating maximum entropy method¹⁶ for which the integrated intensities of 00 l reflections up to $l = 9$ were used.

TEM observation was conducted for the obtained specimens. The powder was dispersed in CH_2Cl_2 and mounted on a holey carbon supporting film. The TEM experiments were conducted mainly by 200-kV TEM (JEM-200CX) operating at 200 kV. The TEM images were recorded at a magnification of approximately 50 000 \times .

Results and Discussion

Ion-Exchange Reaction and Composition. The obtained compositions of the AzAA/LDH complexes

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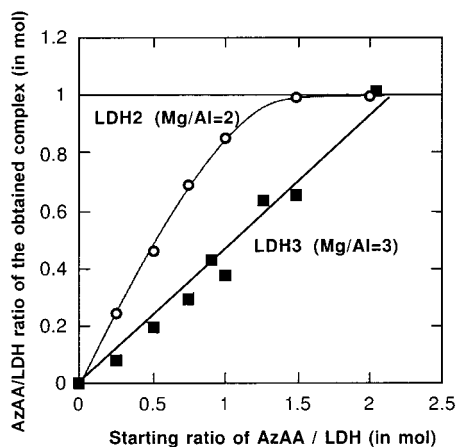


Figure 2. Incorporation of the AzAA into the LDHs at different Mg/Al ratios plotted against the starting ratio AzAA/LDH. Here, the AzAA/LDH ratio indicates the mole ratio of AzAA to Al in LDH.

(resultant AzAA/LDH ratio) prepared by coprecipitation with aging at 60 °C is plotted vs the AzAA/LDH ratio (in mol) of the starting solution (starting AzAA/LDH ratio) in Figure 2. Here, the mole ratios (AzAA/LDH) indicate the AzAA per Al in the LDH, as already mentioned. The plots are shown for the two types of LDHs with different Mg/Al ratios, Mg/Al = 2.0 (LDH2) and Mg/Al = 3.0 (LDH3). The chemical analysis of the Mg and Al elements showed that the Mg/Al ratio of the starting solution was reflected in the value of the obtained intercalates. The Mg/Al mole ratios varied only 5% for all LDH complexes. The Mg/Al ratio differed no more than 3% across the different aging treatments. The AzAA/LDH mole ratios for the obtained complexes were calculated from the CHN chemical analysis data on the basis of the assumption that the AzAA carboxylate anions occupy the interlayer anion sites in replacement of the OH⁻ anions. The amount of organic anions was derived from the observed C, and the water was assumed to be 2.0 per unit formula. The CHN analysis showed the content of organics did not differ because of aging (<4%). The chemical formula of the obtained complexes can be derived from Figure 2. For example, the formula for the AzAA/LDH2 complexes prepared with a starting ratio of AzAA/LDH2 = 1.0 was calculated from the resultant AzAA/LDH ratio as Mg₂Al(OH)₆(AzAA⁻)_{0.85}(OH)_{0.15}·2H₂O, where AzAA⁻ indicates the carboxylate anion form of AzAA. The observed CHN values were C = 34.1, H = 4.82, and N = 5.78 wt %, and the calculated values were C = 34.10, H = 4.69, and N = 5.68 wt %, which are in good agreement. The uptake curves show, for LDH2, that the resultant AzAA/LDH2 ratio is almost the same as the starting ratio; on the other hand, for LDH3, the starting ratio and resultant ratio are different, and only about 50% of the AzAA was incorporated into the interlayer space. Conversion of the starting ratio to the resultant ratio can be conducted using the uptake curves shown in Figure 2. The extent of incorporation is saturated at the theoretical value in both cases (100% replacement of one OH for the formula, Mg₂Al(OH)₆(OH) or Mg₃Al(OH)₈(OH)).

AzAA Orientation in the Interlayer Space and Basal Spacing. The basal spacings of the LDH complexes for each starting AzAA/LDH ratio are listed in

Table 1. Basal Spacings for the Obtained AzAA/LDH Complexes^a

starting AzAA/LDH ratio	LDH2	LDH3
0.00	7.7 Å	7.9 Å
0.25	8.0 Å	8.0 Å
0.50	33 + 8.0 Å	8.0 Å
0.75	23.8 + 33 Å ^b	8.0 Å
1.00	25.6 Å	8 + 22 Å
1.25		8 + 22 Å
1.50	24.8 Å	8 + 22 Å
2.00	25.3 Å	22.5 Å

^a Data for the complexes after aging at 60 °C are listed. ^b Ratios of the 23.8-Å phase and the 33-Å phase changed with aging temperature. The 33-Å phase was dominant for aging at 100 °C.

Table 1. The basal spacing changed as the starting AzAA/LDH ratio increased. At a low starting AzAA/LDH ratio of 0.25, the basal spacings were about 8 Å for both LDHs. This value is close to that of LDH without organic-anion intercalation. For LDH3, the basal spacing was essentially constant up to a starting ratio of AzAA/LDH3 = 0.75, but above this level two phases, 8- and 22-Å phases, appeared. This starting ratio corresponds to the resultant ratio of AzAA/LDH3 = 0.4. For the complex at the starting ratio AzAA/LDH3 = 2.0, only the 22.5-Å phase was observed. This basal spacing indicates a vertical orientation for the AzAA. At this starting ratio, the resultant AzAA/LDH3 ratio was around 1.0 and it means the AzAA is at the maximum amount for the AzAA/LDH3 series. This behavior can be interpreted as follows: The AzAA anions incorporated in the interlayer space exhibited a horizontal orientation at a low AzAA content, and a phase with a vertical orientation of the AzAAs began to appear as the amount of incorporated AzAA increased, as shown in Figure 3.

On the other hand, for LDH2, the basal spacing as large as 33 Å was observed for intercalates at intermediate AzAA/LDH ratios (starting ratios of AzAA/LDH2 = 0.5 and 0.75) after appropriate aging treatment. This basal spacing is much larger than that of LDH2 (25 Å) with a maximum AzAAs content (starting AzAA/LDH2 = 2.0) (Table 1). The basal spacing of 8 Å at AzAA/LDH2 = 0.25 (starting ratio) can be ascribed to a layer with horizontally oriented AzAAs, and that of 25 Å can be ascribed to a layer with vertically oriented AzAAs, as will be discussed in a later section. The 33-Å basal spacing for the AzAA/LDH2 = 0.5 and 0.75 (starting ratios) is close to the sum of the basal spacing for the vertical orientation (25 Å) and that for the horizontal orientation (8 Å), so it can be interpreted as regular alternation of the 8-Å layer and the 25-Å layer, exhibiting *c* = 33 Å supercell, as shown in Figure 4. In other words, this basal spacing can be explained in terms of a second-staging structure.

The basal spacings of complexes with the starting ratio, AzAA/LDH2 = 0.75, varied according to the aging treatment of the resulting suspension. The X-ray powder patterns of the products with AzAAs/LDH2 = 0.75 (starting ratio) are shown in Figure 5 with different aging temperatures. The obtained complexes after 1 night at room temperature showed 23-Å basal spacing, as mentioned before. However, aging treatment of the solution at 60 °C for 1 night led to a mixture of 33- and

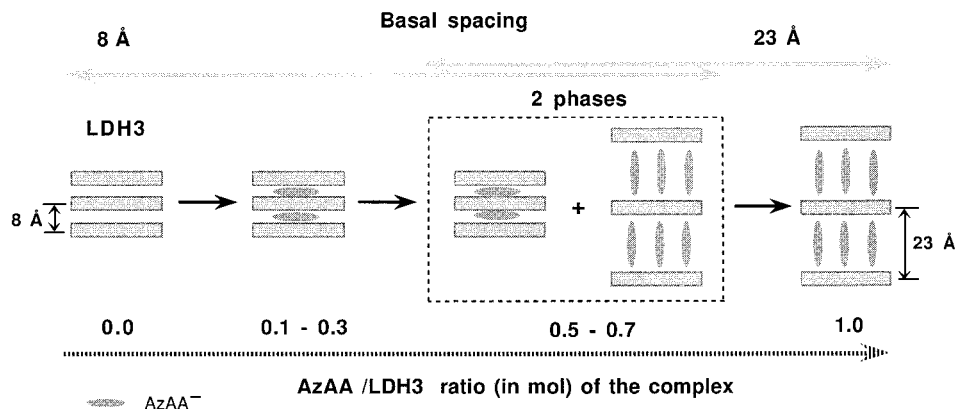


Figure 3. Proposed model for the structure change in the AzAA-LDH3 complexes for different values of intercalated AzAA. LDH3 indicates the LDH with Mg/Al = 3.

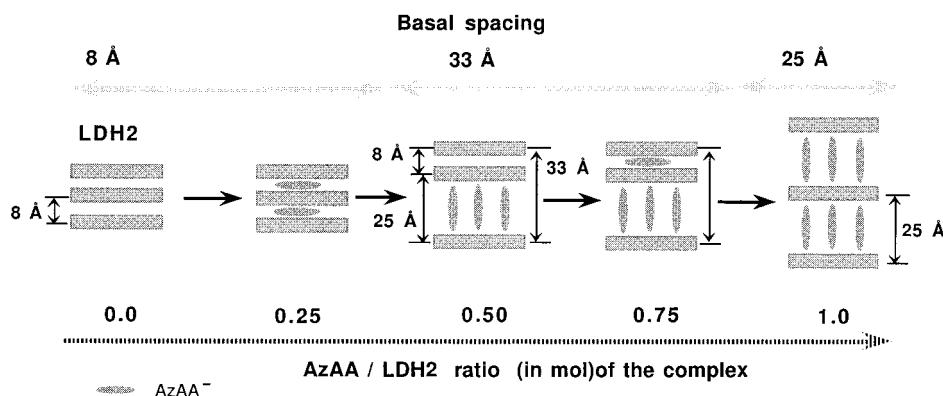


Figure 4. Proposed model for the structure change in the AzAA-LDH2 complexes for different values of intercalated AzAA. LDH2 indicates the LDH with Mg/Al = 2.

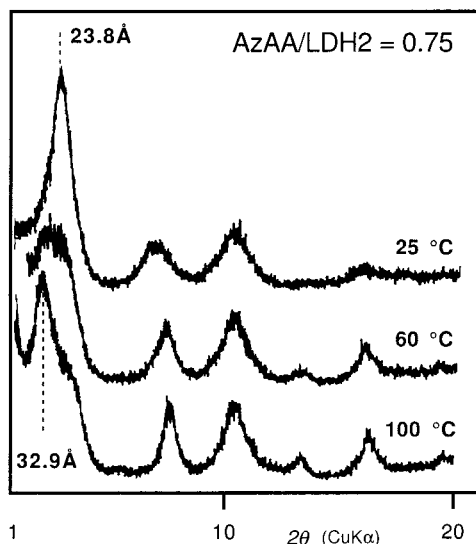


Figure 5. PXRD patterns of the intercalates with AzAA/LDH2 = 0.75 after aging at different temperatures. The second-staging structure is indicated by the peak at ≈ 33 Å.

23-Å phases. The 33-Å phase was dominant for aging at 100 °C. This fact indicates that the higher temperature favors the formation of a 33-Å phase. In the case of AzAAs/LDH2 = 0.5 (starting ratio), only a 33-Å phase was observed together with a small amount of 8-Å phase and the effect of aging treatment was not recognized. For LDH3, two phases (8- and 23-Å phases) were only observed for AzAA/LDH3, and aging did not result in the formation of a second-staging structure.

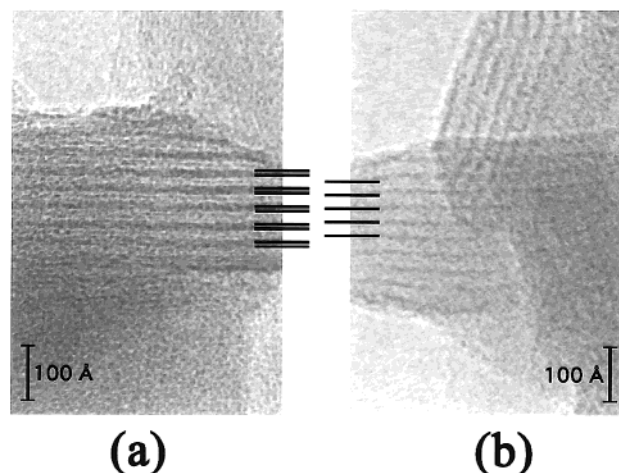


Figure 6. TEM images of (a) the intercalate with the ratio AzAA/LDH2 = 0.75 after aging at 100 °C and (b) the intercalate with the starting ratio AzAA/LDH2 = 2.0 (which corresponds to the resultant ratio AzAA/LDH2 = 1.0) after aging at 60 °C. Bars indicating the Mg-Al hydroxide layers with a stacking sequence of 33 Å (25 + 8 Å) are shown in (a) and those with a stacking sequence of 25 Å are shown in (b).

TEM Observation and Electron Density Map. TEM observation was made for LDH2 complexes with the starting ratio AzAA/LDH2 = 0.75 (100 °C treated), and the starting ratio AzAA/LDH2 = 2.0 (60 °C treated) and the TEM images of layer stackings for the complexes are shown in Figure 6 parts a and b, respectively. These two images were obtained under the same TEM conditions. As already mentioned, the former complex

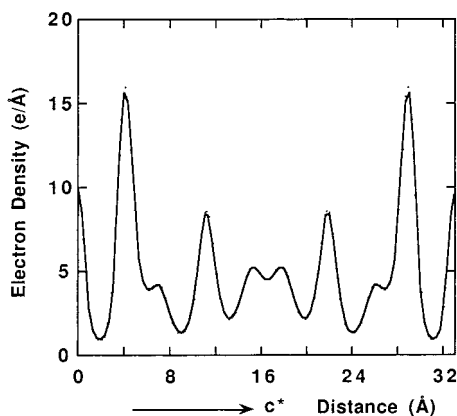


Figure 7. Electron density profile along the c^* direction for the intercalate with the ratio AzAA/LDH2 = 0.75 (aging at 100 °C).

Table 2. Intensity Data^a Used for Electron Density Profile (Figure 7)

	l								
00 l	1	2	3	4	5	6	7	8	9
I_0	100	2	24	38	5	17	3	6	11

^a PXRD data for the intercalate with the ratio AzAA/LDH2 = 0.75 (aging at 100 °C).

has a basal spacing of 33 Å, which is associated with the second-staging structure of the 8-Å layer and the 25-Å layer. The latter complex with starting ratio AzAA/LDH2 = 2.0 (60 °C treated), for which the resultant ratio is AzAA/LDH2 = 1.0, is composed of one type of layer with vertical AzAAs, exhibiting a basal spacing of 25 Å. In Figure 6a,b, the scale is inserted by bars, each of which expresses a Mg–Al hydroxide layer, arranged according to the proposed stacking models of Mg–Al hydroxide layers for each complex. The images are consistent with the above-mentioned structure model of second staging. In the AzAA/LDH2 = 0.75 (100 °C treated) specimens, disordered stacking was also observed in addition to the ordered stacking of the 8- and 25-Å layers. The electron density map for this complex is presented in Figure 7 based on the intensity data listed in Table 2. The electron density ($e/\text{Å}$) is plotted along the c^* axis. The phase of the structure factors were assumed to have the same phase as those calculated for the LDH layer without any organics, and as the value for F_{000} chemical analysis data were used. High electron density peaks due to Mg–Al LDH frame can be recognized at the 4- and 29-Å position. The peaks are 25 Å apart, which is consistent with the model. Between the layers, electron density due to incorporated organic molecule can be seen. The phase for (006) reflection was arbitrarily assigned to be plus since this reflection calculated for the LDH layer is very small.

Dimensions of AzAA and Its Alignment in the Interlayer Space. The dimensions of the AzAA were estimated based on the van der Waals radii and the molecular structure (Figure 8a). The molecular structure with a minimum energy was calculated by using the semiempirical molecular dynamics method (MM2, Chem3D, CambridgeSoftware). The long axis length is about 15 Å. As the layer thickness of LDH is estimated to be 5 Å on the basis of the positional parameters of

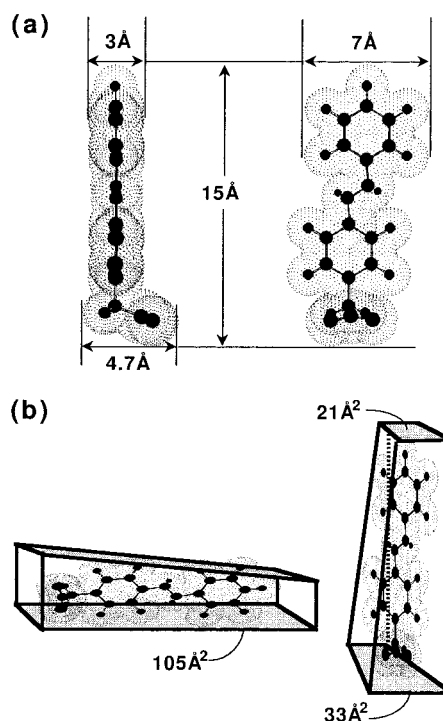


Figure 8. (a) The dimensions of the AzAA anion and (b) the areas occupied by different AzAA orientations.

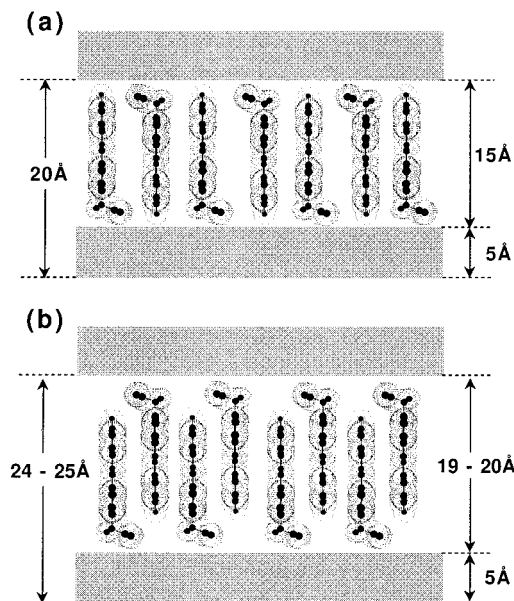


Figure 9. Estimations of basal spacing for vertical orientations in the cases of (a) long, and (b) short intermolecular distances.

pyroaurite by Allmann,¹⁷ the basal spacing would be 20 Å for a layer with vertical AzAA. The observed basal spacing was 22–25 Å, which is larger than this value. Two parallel AzAAs arranged horizontally in the interlayer space may be assumed as a model; however, as the thickness of AzAA is 3–4.5 Å, then a basal spacing of 11–14 Å would be expected by adding the thickness of the LDH layer (5.0 Å). This is far less than the observed value, and four parallel AzAAs arranged horizontally in the interlayer space would not be realistic. Membrane-like bilayer arrangement with tilted

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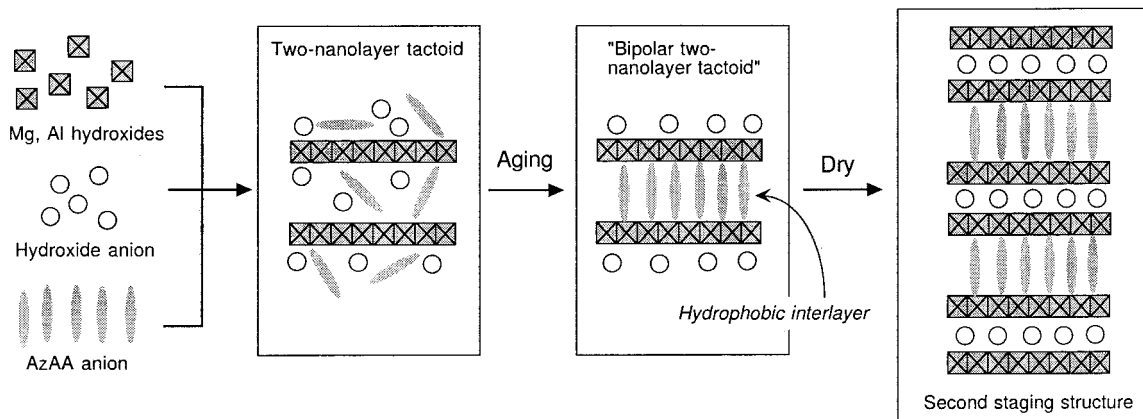


Figure 10. Scheme of the formation of second staging, via tactoids for the AzAA/LDH2 complexes prepared by a coprecipitation method.

molecules may be another possibility. However, preliminary UV–Vis spectroscopic measurement showed that the absorption maximum was at 328 nm (π – π^* transition) for aqueous solution of AzAA sodium salt (0.1 mM) and that no apparent band shift was observed for AzAA in the complexes with AzAA/LDH3 = 1.5 and AzAA/LDH2 = 1.5 (λ_{\max} = 333 nm). No apparent spectral shift in the present case may indicate an intermediate state between tilted bilayer assembly and interdigitated arrangement.¹⁸ Such “tilt interdigitated antiparallel structure” would be another possibility, but there are many factors that affect the absorption spectrum. As monolayer interdigitated structure is commonly observed,^{19,20} it would not be unreasonable to assume interdigitated structure with nearly vertically oriented molecules.

The observed basal spacing can be explained by a vertical model considering the dimensions and shape of the AzAA. The area per unit minus charge can be calculated from the crystallographic data of LDH:¹⁷ 25 Å² for LDH2 and 33 Å² for LDH3. From the dimensions of AzAA, the cross-section area perpendicular to the long axis is 21 Å² (3 × 7 Å) for the phenylazophenyl part. However, when the fact that the carboxylate group is tilted from the long molecular axis is taken into consideration, an anionic part of AzAA anion would occupy an area of 33 Å² (4.7 × 7 Å). AzAA anions are considered to be arranged in an antiparallel fashion (Figure 9a), so a pairing of an AzAA with an area of 21 Å² and an AzAA with an area of 33 Å² together would occupy an area of 54 Å². The average area per AzAA will be 54 Å²/2 = 27 Å², which is compatible with the area per unit charge for LDH3. So the AzAA anions might be arranged in such a way that they interact little laterally in LDH3 (Figure 9a). On the other hand, this area (27 Å²) is larger than the area available in LDH2. So, for LDH2, each AzAA anion could not be separated enough, causing sliding of the antiparallel AzAA layers to reduce the lateral interaction as shown in Figure 9b, while maintaining the interdigitated structure. Expansion of interlayer space caused by the slide of organic layers was observed for the layered hydroxide system¹⁹ and

also for monolayer carboxylates in stilbene–LDH intercalates.²⁰ This may be the reason the basal spacings of the LDH2 and LDH3 complexes with the vertically oriented AzAAs showed a difference.

The change in the arrangement of the AzAAs at the interlayer space caused by the AzAA/LDH ratio can also be explained in terms of the dimensions of the AzAA. For the horizontal orientation, the AzAA covers 105 Å² (Figure 8b), so the ratio to unit charge area for LDH2 (25/105 Å²) is 0.24. This means that the maximum content of horizontal AzAA in LDH2 would be expected to be about 24% (AzAA/LDH2 = 0.24). In reality, in the complexes with starting AzAA/LDH2 = 0.25, whose resultant ratio is also 0.25, horizontal orientation was observed. Above this ratio, another arrangement of the AzAAs occupying less area would be expected to take place. The following scheme can be expected. At AzAA/LDH2 = 0.5, it is predicted that one layer will be occupied by vertical AzAA and another will contain little or no AzAA. At 0.75, one layer will be occupied by vertical AzAAs and another layer will be occupied by horizontal AzAAs. Beyond this point every interlayer space is expected to contain only one type of AzAA with vertical orientation until the interlayer space reaches full occupation (AzAA/LDH2 = 1.0).

For LDH3, the change in basal spacing can also be explained in the same way. As the horizontally oriented AzAA occupies 105 Å², the maximum occupation of this orientation is about 0.31 for LDH3 (33/105 Å²). This ratio, the resultant AzAA/LDH3 of 0.31, corresponds to starting ratio AzAA/LDH3 = 0.8, as can be seen in Figure 2. So a horizontal alignment of the AzAAs is expected for starting ratios AzAA/LDH3 = 0.8, and this was the case (Table 1). Above this level, another alignment would take place to incorporate more AzAAs. In fact, 8- and 22-Å phases could be observed above the starting ratio AzAA/LDH3 = 0.9. Thus, the change in alignment and basal spacing can be explained by simple geometric considerations. Meyn et al.²¹ pointed out that the interlayer arrangement depends strongly on the area available to each interlayer anion in LDH, and this is also the case with the present system.

The reason staging takes place only for high-charge density LDH2 cannot, however, be explained merely in terms of geometrical considerations. Ijdo and

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Pinnavaia¹¹ studied the factors to obtain alternation of two types of interlayer space for alkylammonium ions and a synthetic mica system prepared by ion exchange in suspension. They claim that (i) the hydrophobic binding effect of the organic part and (ii) the size of the ammonium cation (headgroup "footprint") compared to layer-charge density are the factors for controlling the staging phenomenon. They assumed that because of these two factors, inorganic cations would be excluded from the interlayer space of a two-layer nanoclay particle or "tactoid", leading to the formation of bipolar two-nanolayer tactoids in an aqueous suspension with organic hydrophobic mid-interlayer space (Figure 10) and that thus formed tactoid structure would give rise to staging after being dried.¹¹ In the present system, the anionic carboxylate anion is not large, so the concept of footprint effect does not work in the strictest sense. However, the size of the AzAA bound to the layer surface is determined not only by the carboxylate anion part but also by the neighboring benzene ring, leading to a broad exclusion area. So a size effect similar to the footprint effect may work in the present system. This effect is much greater for the LDH2 system than for the LDH3 because of the higher layer charge in the LDH2. The fact that staging behavior is favored by LDH2 can be understood in terms of the layer-charge and anion-size relation. Another observation that aging at the higher temperature favored staging is in contrast with graphite systems in which staging is favored at lower temperatures. This phenomenon can be explained by

assuming the formation of bipolar two-nanolayer tactoids,¹¹ as illustrated in Figure 10. Initially formed LDH tactoids in which the AzAA anions are randomly adsorbed change their structure by rearrangement of the AzAAs caused by higher temperatures, leading to a more regular structure—second staging. This mechanism is different from the Rudolff mechanism that Fogg et al.¹³ adopted for anion-exchange intercalation reaction of LDH. According to the Rudolff mechanism, which was originally proposed for the staging phenomenon in the graphite systems,²² the second staging is caused by filling of every second layer during intercalation. In the present case, the tactoid hypothesis would be more plausible, considering the coprecipitation method used for synthesis, that is, the direct synthesis of the LDH host frame in the presence of organic anions. Our preliminary experiment showed the wet gel just after aging shows no reflection peaks by PXR, but reflections began to appear and became stronger upon drying.

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