Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **24:** 341–351, 1996.

Variable Interlayer Distance of Intercalates of Naphthalenedisulfonate Isomers in Hydrotalcite-Like Zn and Al Layered Double-Hydroxides

EIJI KANEZAKI
Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima 2-1, Tokushima 770, Japan.

(Received: 4 December 1995; in final form: 16 April 1996)

Abstract. Three isomers of naphthalenedisulfonates (naphthalene-2,6-,-1,5- and -2,7-disulfonates; abbreviated as N26DS, N15DS and N27DS, respectively, and collectively abbreviated as NijDS) are intercalated in the interlayer region of Zn and Al layered double-hydroxides (Zn/Al-LDH). The intercalated products are obtained under weak alkaline conditions as precipitates from reaction mixtures containing one of the isomers and calcined powder prepared by using carbonate-intercalated Zn/Al-LDH. When N26DS or N15DS is intercalated, two solid phases are observed which have different values of basal spacing in powder X-ray diffraction (XRD) patterns, whereas only one phase appears when N27DS is intercalated. The different basal spacing results from one of two alternate orientations taken by the interlayer NijDS. One of the two phases appears exclusively in XRD patterns, although the other is produced together with a by-product. A more closely packed orientation is suggested for the interlayer guest molecules in the latter phase. The solid state chemistry has been investigated using UV-visible diffuse reflection (DR) spectroscopy, differential thermal analysis/thermogravimetry (DTA/TG) and X-ray photoelectron spectroscopy (XPS).

Key words: Hydrotalcite, intercalation, layered compound, layered double hydroxides.

1. Introduction

Hydrotalcite (HT) is a layered double hydroxide (LDH) and has a layered structure where carbonate dianions are intercalated in the interlayer gallery spacing between brucite-like layers of Mg/Al-LDH [1]. The structure of the layers, $[\mathrm{M}_a^{\mathrm{II}}\mathrm{M}_b^{\mathrm{III}}(\mathrm{OH})_{z(a+b)}]^{+b}$ where M^{II} and $\mathrm{M}^{\mathrm{III}}$ are di- and trivalent metal cations, respectively, is maintained when the Mg^{2+} ions in the layers of HT are replaced isomorphously by Zn^{2+} ions producing positively charged layers of Zn/Al-LDH in a synthetic HT-like compound [2, 3]. In the interlayer region, there are water molecules and some inorganic anions which compensate the positive charge of the layers. It has been reported that aliphatic [2] and aromatic [4–10] molecular dianions are intercalated in HT and HT-like compounds by ion exchange of the interlayer inorganic anions. When these large organic ions are intercalated, an increase of the basal spacing is usually observed in powder XRD patterns. On intercalation of

N15DS* between layers of Zn/Al-LDH, it has been reported that the basal spacing disagrees with the value previously published [5]. We have recently reported that two values of the basal spacing are observed when 9,10-anthraquinone-2,6-disulfonate (AQ26) is intercalated between layers of Mg/Al-LDH [10]. The two values of the basal spacing originate from the lower symmetry in the structure of intercalating AQ26 compared to the exchangeable inorganic ions between layers of Mg/Al-LDH. In other words, since organic molecules generally have spatial anisotropy in their dimension and since the dimension of the interlayer molecules being measured along the direction perpendicular to the layer surface is reflected in the magnitude of the interlayer distance of the intercalated products, the magnitude of the interlayer distance consequently depends on the orientation of the interlayer organic molecules. An examination of these synthesis gives possible orientations of the interlayer molecules and thereby information on the interaction(s) between the molecules and other component(s) in the products as well as understanding the properties of the products for potential use.

In this paper, the two values for the basal spacing are described in relation to the orientation of the interlayer molecules when N26DS* or N15DS* is intercalated separately between layers of Zn/Al-HT together with results for the N27DS*-intercalated product.

2. Experimental

The starting material was Zn/Al-LDH which had interlayer CO_3^{2-} ions and which was prepared by the hydrolysis of $ZnCl_2$ and $AlCl_3$ (Kanto Chemicals) with the ratio Zn/Al = 2 in air at room temperature. The pH of the reaction mixture was maintained at 11–12 by using NaOH and Na_2CO_3 (Kanto Chemicals). The resulting while solid has the chemical composition of $ZnAl_{0.50}(OH)_{3.00}(CO_3)_{0.25} \cdot 0.61H_2O$ and was used in the synthesis of all intercalated products in this study. When the Zn/Al ratio was increased from 2 to 4 in the preparation, the analytical ratio Zn/(Zn+Al) of the corresponding solid only increased from 0.67 to 0.70. The starting material exhibits the typical XRD pattern of HT (not shown); the basal diffraction at $2\theta = 11.62°$ ($d = 0.761$ nm) is followed by a sequence of ($00l$)-type diffractions [5]. Although this XRD pattern disappeared when the starting material was calcined at 500 °C for 3 h in air, the pattern reappeared on the reconstruction of the layered structure of HT when the calcined powder was hydrolyzed in deionized water at room temperature. Intercalation of NijDS takes place when the layered structure reappears in aqueous solutions of NijDS. All sources of NijDS in this study were reagent grade sodium salts from Tokyo Kasei and were used as received. The calcined powder was added to an aqueous solution containing one of the organic salts at room temperature with vigorous stirring whilst keeping the pH between 11 and 12 in air, followed by ageing for 18 h at 73–74 °C. The white precipitate was

---

* N15DS, N26DS and N27DS, collectively abbreviated as NijDS, refer to the 1.5, 2.6 and 2.7 isomers of naphthalene disulfonate, respectively.

collected, washed using deionized water until a negative test for Cl^- with Ag^+ was observed in the filtrate and finally dried overnight at 80 °C. The chloride content in these products was commonly less than 0.1% of the total sample mass and is thus omitted from the chemical formulae in Table I.

XRD, XPS and DR spectroscopic measurements were carried out as described previously [5,11]. A semiempirical MO calculation with the MOPAC/PM3 program [12] was used to estimate the optimal geometries of the guest organic anions with respect to bond lengths, bond angles and dihedral bond angles as deduced from the lowest value of the formation enthalpy (ΔH_f) as used previously [5].

3. Results and Discussion

Figure 1 exhibits two XRD patterns of the N26DS-intercalated products. It has been reported that the unit cell of HT has hexagonal symmetry with a lattice constant $a_0 = 0.306$ nm and with the c axis perpendicular to the layers [2, 13]. The XRD patterns of the NijDS-intercalated products were analyzed on the assumption that the unit cell symmetry and the a_0 dimension was the same as those of HT but that the dimension of the other lattice constant c_0 differs among the products. The basal diffraction appears at $2\theta = 5.74°$ ($d = 1.538$ nm) and is associated with some prominent (00l)-type diffractions in Figure 1A (the 15 Å phase). Indexing of the XRD pattern in this figure indicates that only one phase exists and that the predominant crystal growth occurs in the direction parallel to the c axis in this solid sample. The latter observation points out well developed stacking of the Zn/Al-LDH layers along this axis [1, 2]. The basal diffraction shifts to a slightly smaller angle of $2\theta = 5.18°$ ($d = 1.705$ nm) in Figure 1B (the 17 Å phase). The 17 Å phase of the N26DS-intercalated product was obtained when the amount of the organic salt was increased relative to that of aluminum in the calcined powder; the ratios being (organic salt)/Al = 5 and 1 for the 17 Å and the 15 Å phases, respectively. Although the intense (00l) diffraction of the 17 Å phase is also associated with some (00l)-type lines, an additional diffraction sequence (marked with asterisks in Figure 1B) is present. Since the additional sequence agrees with the XRD pattern of the starting material, it is concluded that the synthetic condition for the 17 Å phase of the N26DS-intercalated products is similar to the condition for the carbonate-intercalated product in which interlayer CO_3^{2-} ions are originally solvated species in the reaction mixture.

In the XRD pattern of the 15 Å phase of the N15DS-intercalated products (Figure 2A) the basal diffraction appears at $2\theta = 5.82°$ ($d = 1.517$ nm) and in the pattern of the 17 Å phase (Figure 2B) the diffraction appears at $2\theta = 5.24°$ ($d = 1.685$ nm). Although both phases in Figures 2A and 2B exhibit well developed stacking of the layers, the 17 Å phase in the latter figure appears together with the carbonate-intercalated product as observed in Figure 1B. Since only the 15 Å phase of the N15DS-intercalated products is obtained after leaving the precipitate in the reaction mixture for 40 days, it is suggested that this phase is thermodynamically

Table I. Summary of results and synthetic conditions of NijDS-intercalated products.

Guest	l_M[1]/nm	l_L[2]/nm	$\left[\frac{\mathrm{NijDS}}{\mathrm{CO_3}}\right]$[3]	Zn : Al : NijDS[4]	$\mathrm{M^{II}/M^{III}}$[5]	Notes	
N26DS	1.266	1.23	0.67	4 : 2 : 5	Zn/Al	17 Å phase	This work
		1.06	0.56	4 : 2 : 1	Zn/Al	15 Å phase	Kanezaki *et al.* [5]
N15DS	1.205	1.21	0.56	4 : 2 : 1	Zn/Al	17 Å phase	Kanezaki *et al.* [5]
		1.04	0.39	4 : 2 : 1	Zn/Al	15 Å phase	This work
		1.03	–	–	Mg/Al	15 Å phase	Drezdson [4]
		1.03	–	–	Zn/Al	15 Å phase	Meyn *et al.*[9]
		1.04	–	–	Zn/Cr	15 Å phase	Meyn *et al.* [9]
		1.08	–	–	Ca/Al	15 Å phase	Meyn *et al.* [9]
N27DS	1.208	1.17	0.26	4 : 2 : 1	Zn/Al	17 Å phase	Kanezaki *et al.* [5]

[1] Molecular size: twice the anionic radius of oxygen (0.28 mm) plus the interatomic distance between two anionic groups of an aromatic dianion whose geometry is optimized in MO calculation.

[2] Interlayer distance: the interplanar spacing *d*(001) obtained in XRD patterns minus the thickness of a layer (0.48 nm).

[3] Molar ratio of intercalating NijDS and CO_3^{2-} based on the chemical analysis of intercalated products with the composition of the layer $[ZnAl_{0.50}(OH)_{3.00}]$ and with compositions of the interlayer being $(CO_3)_{0.15}(N26DS)_{0.10}$, $(CO_3)_{0.16}(N26DS)_{0.09}$; $(CO_3)_{0.16}(N15DS)_{0.09}$, $(CO_3)_{0.18}(N15DS)_{0.07}$ for the 17 Å phase and for the 15 Å phase of N26DS-intercalated and of the N15DS-intercalated products and $(CO_3)_{0.20}(N27DS)_{0.05}$ for the 17 Å phase of the N27DS-intercalated product. Water and chloride are omitted.

[4] Molar/atomic ratio in preparation.

[5] Divalent (M^{II}) and trivalent (M^{III}) metal ions within layers.

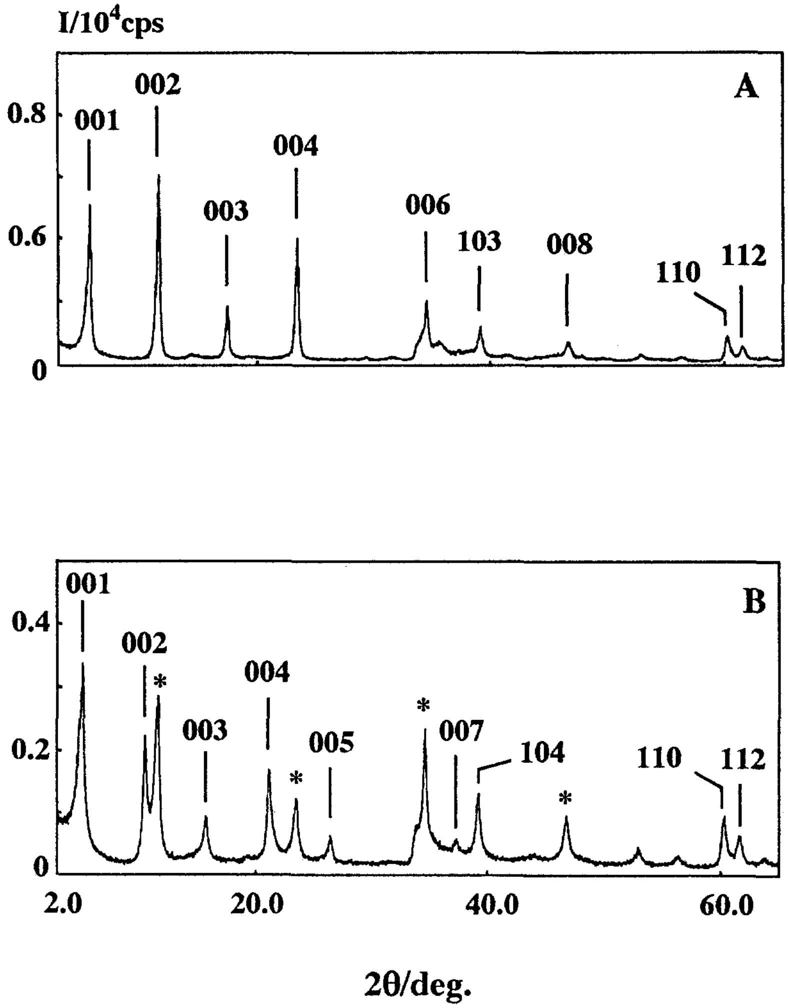

Figure 1. XRD patterns of N26DS-intercalated products, using Ni-filtered CuK_{α_1} line (λ = 0.15405 nm) in which the diffraction angle was scanned stepwise by 0.02°: (A) the 15 Å phase with diffraction lines at 2θ=5.740° (001), 11.58° (002), 17.44° (003), 23.36° (004), 29.38° (005), 34.54° (006), 41.50° (007), 46.74° (008), 52.94° (009), 60.20° (00 10) and 61.50° (110): (B) the 17 Å phase with lines at 2θ = 5.18° (001), 10.50° (002), 15.72° (003), 21.12° (004), 26.42° (005), 37.32° (007), 53.12° (00 10) and 60.22° (110); lines with asterisks are those of the host Zn/Al-HT without interlayer aromatic molecules.

more stable than the 17 Å phase. This 15 Å phase has been observed within several kinds of LDH by Drezdson [4] and Meyn *et al.* [9]. In contrast, only the 17 Å phase is observed in the XRD pattern (not shown) of the N27DS-intercalated product, in which the basal diffraction appears at 2θ = 5.34° (d = 1.654 nm). It should be noted that the magnitude of the interlayer distances of the 17 Å phases of all the NijDS-intercalated products in Table I is in good agreement with the estimated

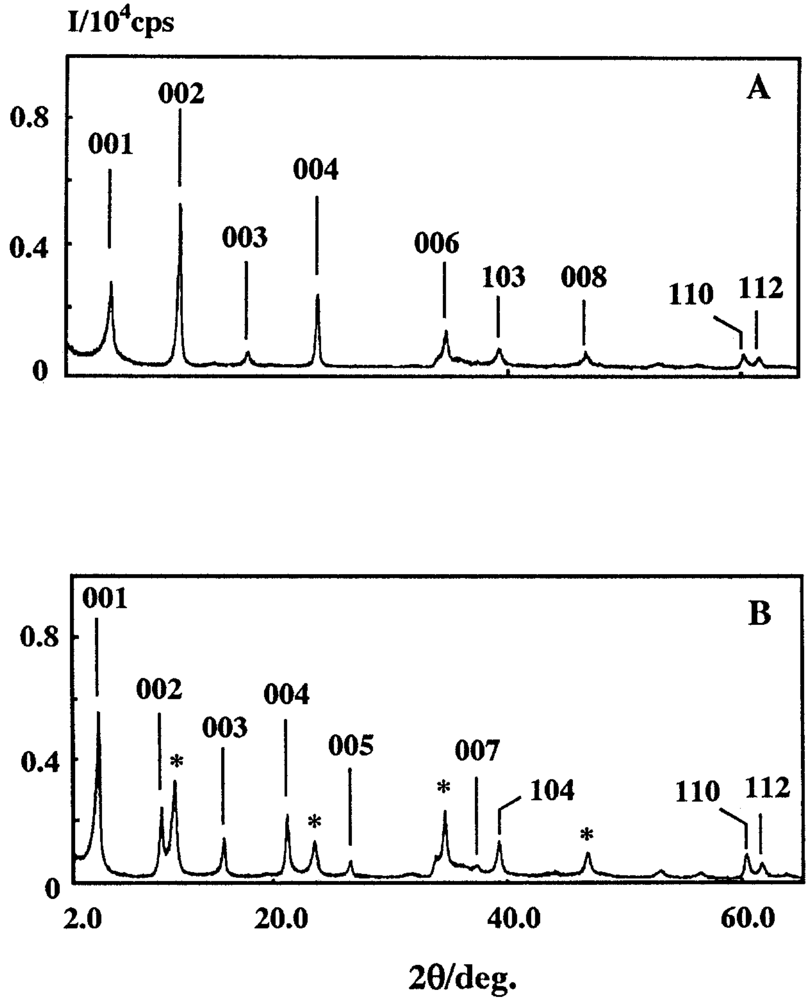

Figure 2. XRD patterns of N15DS-intercalated products using the same experimental condition as in Figure 1: (A) the 15 Å phase with diffraction lines at 2θ = 5.820° (001), 11.68° (002), 17.58° (003), 23.48° (004), 29.24° (005), 35.60° (006), 60.20° (110) and 61.72° (00 10); (B) the 17 Å phase with lines at 2θ = 5.24° (001), 10.54° (002), 15.80° (003), 21.18° (004), 26.54° (005), 37.36° (007), 56.48° (00 10) and 60.26° (110); lines with asterisks are the same as those in Figure 1.

molecular size of the individual guest organic anions using MO calculations. This result is significant and will be discussed later.

In the DR spectrum (not shown) of the 17 Å phase of the N26DS-intercalated products, two maxima are located at $\lambda_{\text{max}} = 277$ nm and at $\lambda_{\text{max}} = 314$ nm which are assigned as a ${}^1B_{2u}(\pi, \pi^*)$ and a ${}^1B_{3u}(\pi, \pi^*)$ transition, respectively, in the naphthalene moiety [14]. This profile in the DR spectra is commonly observed in all the spectra of NijDS-intercalated products in this study within experimental error. Therefore, it strongly suggests that the interlayer organic anions are stabilized by the conjugated π-electron framework and retain the planar molecular skeleton of the naphthalene moiety.

A typical wide scan XPS spectrum of the 15 Å phase of the N26DS-intercalated product (Figure 3) shows several peaks which are assigned to core level electrons emitted from Zn, Al, C, S and O atoms of the solid samples [15]. Since the guest ions in the interlayer region and the Al^{3+} ions in the layers are attracted electrostatically, we examined the binding energy of the Al $2p$ electron, E_b(Al $2p$). In the starting material with interlayer carbonate, E_b(Al $2p$) is 74.2 ± 0.6 eV (1 eV = 1.602×10^{-19} J) which agrees with that of the octahedrally coordinated Al^{3+} ions previously reported [16]. No significant shift of E_b(Al $2p$) is observed after intercalation of NijDS, within experimental error; E_b(Al $2p$) of the 15 Å and of the 17 Å phases are 74.9 ± 0.6 and 75.0 ± 0.6 eV for the N26DS-intercalated products, 74.6 ± 0.7 and 74.9 ± 0.6 eV for the N15DS-intercalated products, respectively, and 74.4 ± 0.6 eV for the N27DS-intercalated product. Furthermore, it is concluded that E_b(Al $2p$) does not depend on the magnitude of the basal spacing in this study. Since the binding energy is a good measure of the chemical status of metals [15], it is concluded that the aluminum ions in the layers still exist as trivalent cations and are coordinated octahedrally in all phases of the NijDS-intercalated products. In other words, the two values for the basal spacings of the N26DS- and N15DS-intercalated products do not originate from any change in the chemical status of the Al^{3+} ion in the layer. A full discussion of the XPS results will be reported elsewhere.

Figure 4 shows a typical DTA/TG thermogram of the N27DS-intercalated product. Two prominent endotherms (at 195.3 °C and at 282.8 °C) and two exotherms (at 519.9 °C and at 565.2 °C) are seen in the DTA curve. This profile agrees well with that of the 15 Å phase of the N26DS-intercalated product [5] where two endotherms at 185.3 °C and at 308.4 °C were both assigned to the elimination of water and CO_2, and exotherms at 486.8 °C and at 564.7 °C to thermal decomposition of N26DS at the outer surface and in the interlayer region, respectively. The result of the previous study leads us to the parallel conclusion that the two endotherms are assigned to the elimination of water and CO_2 molecules and that the two exotherms are due to the decomposition of N27DS anions at the outer surface (519.9 °C) and in the interlayer region (565.2 °C). It is important that we thermally distinguish two anion sites at which NijDS ions locate; the outer surface and the interlayer region [5]. The total weight loss of the sample in the temperature range up to 800 °C is 35.8%, which corresponds to the sum of water, carbonate and N27DS contents (36.0%) as estimated from the result of the chemical analysis in Table I. All the NijDS-intercalated products give the same DTA/TG profile, which indicates that the peak locations are insensitive both to the difference in the magnitude of the basal spacing and to the kind of guest isomer.

Early crystallographic work by Allman revealed that the LDH layer is built up by sharing one edge of the octahedron unit in which a metal cation is centered and

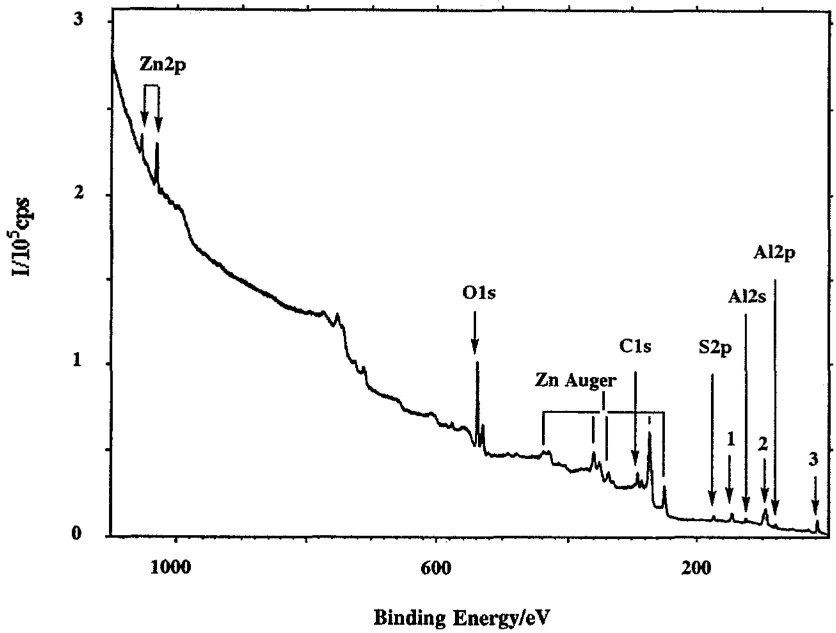

Figure 3. A wide scan XPS spectrum of the N26DS-intercalated product obtained by using a Mg cathode ($h\nu = 1253.6$ eV) and an X-ray gun (10 kV/30 mA) under reduced pressure (10^{-5}–10^{-6} Pa). A reference peak location of E_b (C 1*s*) = 285.0 eV is used in peak assignment which is indicated by arrows. (1) Zn 3*s*, (2) Zn 3*p* and (3) Zn 3*d*.

is coordinated by six —OH^- groups [13]. In his conclusion, the interlayer CO_3^{2-} ion has the conformation in which the molecular plane of the ion lies parallel to the two-dimensional layers; the magnitude of the interlayer distance is thus essentially equal to the diameter of the O^{2-} ion. Although an orientation of interlayer organic anions perpendicular to the layer surface was concluded in earlier studies [4, 6, 7], a tilted orientation of the anions has been suggested recently [5, 8–10] when basal spacings of the intercalated products in XRD patterns are smaller than the molecular sizes of the anions. In Table I, l_L of the 17 Å phase agrees with l_M in all the NijDS-intercalated products; this result strongly suggests that the interlayer NijDS anion in this phase takes the bridging orientation which links a pair of Al^{3+} ions in the neighboring layers like a zip fastener on these two layers. The line that connects two anionic oxygen atoms (the O—O line), each of which belongs to different sulfonate groups in one bridging NijDS, is parallel to the *c* axis in this orientation. In the 15 Å phase, however, the interlayer distance is smaller than the molecular size of the guest in Table I. A plausible explanation is displayed in Figure 5 for the case of interlayer N15DS; the guest molecule has an orientation in which the O—O line is not parallel to the *c* axis. It is the author's opinion that the variation in the magnitude of the basal spacing is caused by the variation in the magnitude of the enhanced interlayer distance and that the latter variation originates from

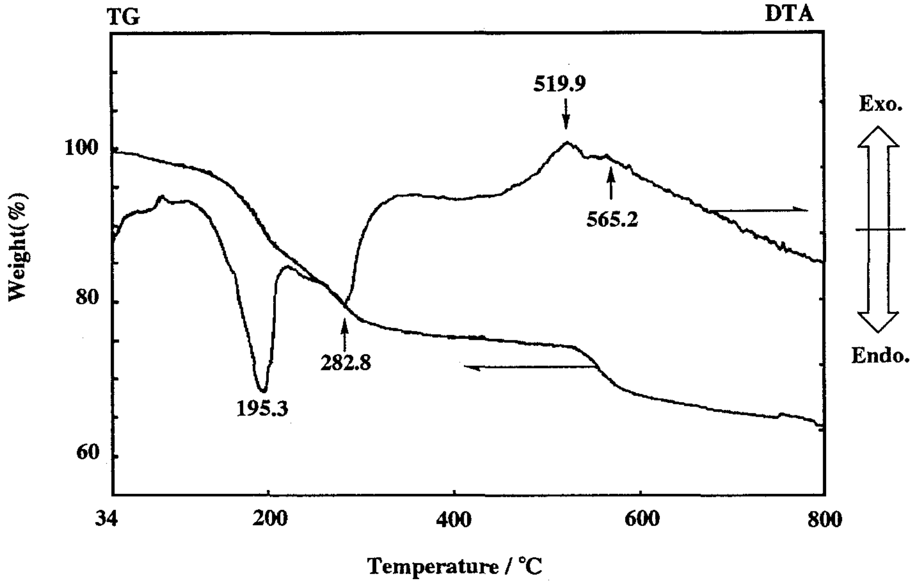

Figure 4. DTA/TG analysis of the N27DS-intercalated product in the range of (room temperature) $\leq T \leq 800$ °C under an atmosphere of N_2 with a heating rate of 10° C min^{-1} and using α-Al_2O_3 as a reference. Temperature values are also included for major peaks which are indicated by arrow.

an alternate orientation by the interlayer molecular anions in the cases of N26DS and N15DS. The variation in the basal spacing is not due to the difference in the thickness of the layer because this variation is so small in both cases (1.7 Å) that it cannot be explained by the change of the stacking number of the octahedron unit.

In the 15 Å phase, a pair of Al^{3+} ions which are linked by one N15DS molecule do not locate directly opposite to each other but are separated in length by $R = 0.60 \pm 0.09$ nm measured along the inner surface of the layers (Figure 5) although $R = 0$ in the 17 Å phase. The separation in Figure 5 agrees with the value of $R = 0.68 \pm 0.05$ nm previously reported for the case of the interlayer N26DS anion in the 15 Å phase [5] and both values are approximately equal to twice the interatomic distance between two adjacent metal ions (R_0 = 0.312 nm [17]) in the layers of Mg/Al-LDH. If we assume that interatomic distances in the layers of Mg/Al-LDH and in the layers of Zn/Al-LDH are the same, it is interesting that only two values of the ratio R/R_0 are observed; $(R/R_0) = 2$ for the 15 Å phases and $(R/R_0) = 0$ for the 17 Å phases. Although the author cannot propose a reason why a value of 1 for the ratio is missing, it is assumed that the reason may be steric hindrance due to the bulky naphthalene moiety.

In Table I, the chemical compositions of the interlayers in intercalated products are listed; both ions of CO_3^{2-} and NijDS coexist in all solid samples which are prepared in this study. It has been reported that some kinds of hydrotalcite with interlayer carbonate have been synthesized [1, 2]; the interlayer distance (ca. 3

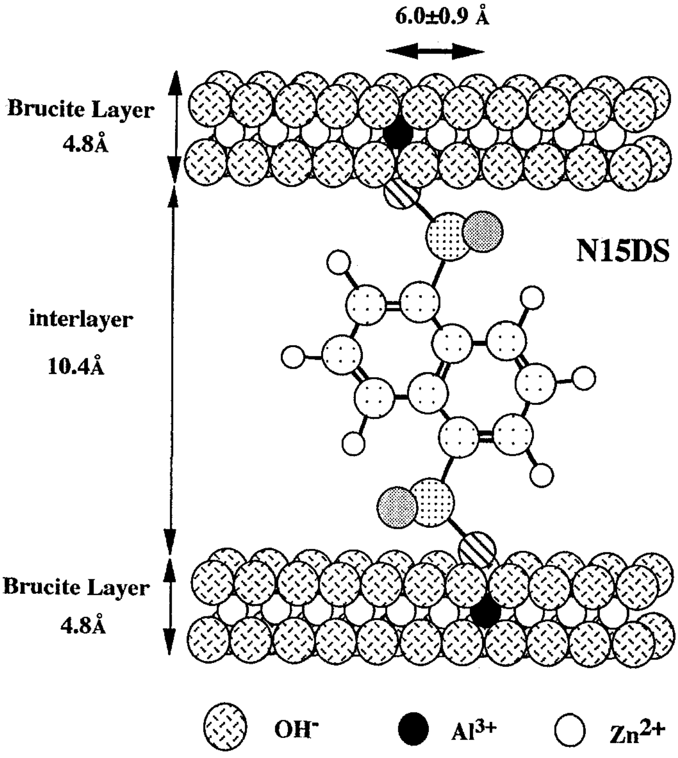

Figure 5. A plausible orientation of the interlayer N15DS between two layers of Zn/Al-LDH in the 15 Å phase; other anions and water molecules are omitted.

Å), which is equal to the molecular size of carbonate, is much smaller than the molecular size of NijDS in this study. Therefore, even when both carbonate and NijDS ions coexist in the same interlayer, we cannot recognize the coexistence of two ions in XRD patterns because NijDS ions act as pillars between two LDH layers. This is the case which we observe in the 15 Å phases. In contrast, when two kinds of intercalated product are formed as a mixture, one is the NijDS-intercalated product and the other is CO_3-intercalated product, we can recognize this situation in XRD patterns. This is the case which we observe in the 17 Å phases. No evidence to support the presence of a superlattice has been observed so far. The ratio NijDS/CO_3 is always larger in the 17 Å phase than in the 15 Å phase for the N26DS- and N15DS-intercalated products. Considering that the 17 Å phases of these two intercalated products are produced together with the carbonate-intercalated product and that the compositions of the 17 Å phases in Table I are thus of a mixture of them, the real ratio in the pure phase is larger than the value listed in Table I for both 17 Å phases. We therefore conclude that the guest molecules in the 17 Å phase are packed in the interlayer region more closely than in the 15 Å phase, which is realized by taking the orientation of the guest molecule in the 17 Å phase as described above. The reason why more than one basal spacing is not observed in the N27DS-intercalated product is not known. In the previous work, we reported that only the 15 Å phase was observed when N26DS is intercalated and that only the 17 Å phase was observed when N15DS or N27DS was intercalated [5] as listed in Table I. Together with the results of Drezdzon [4] and of Meyn *et al.* [9], this study reveals that the duality in the magnitude of the interlayer distance due to the orientation change of the interlayer molecules is commonly observed when N26DS or N15DS is intercalated between layers of Zn/Al-LDH as well as when AQ26 is intercalated between layers of Mg/Al-LDH [10]. Although a precise, quantitative investigation is necessary in order to obtain a more exact and total view of the orientation of molecular anions between layers of LDH, it is important to note that the magnitude of the basal spacing can be changed by means of controlled preparation conditions. With this variable magnitude of the basal spacing, we would be able to design materials with desirable pore sizes in the mesospore region, which is valuable in reaction catalysis and in adsorption technology.

Acknowledgment

The authors are indebted to Dr. Kenta Ooi, Shikoku National Industrial Research Institute (SNIRI), Takamatsu, Japan, for kind permission to use the XRD facility.

References

1. F. Cavani, F. Trifiro, and A. Vaccari: *Catalysis Today* **11**, 173 (1991); A. Roy, C. Forano, K.E. Malki, and J. Besse: in M.L. Occelli and H. Robson (ed.), *Expanded Clays and Other Microporous Solids*, Ch. 7, Van Nostrand Reinhold, New York (1992).
2. S. Miyata: *Clays Clay Miner.* **23**, 369 (1975).
3. A. Bhattacharyya and D.B. Hall: *Inorg. Chem.* **31**, 3869 (1992).
4. M.A. Drezdzon: *Inorg. Chem.* **27**, 4628 (1988).
5. E. Kanezaki, K. Kinugawa, and Y. Ishikawa: *Chem. Phys. Lett.* **226**, 325 (1994).
6. K. Chibwe and W. Jones: *J. Chem. Soc., Chem. Commun.* 926 (1989).
7. I.Y. Park, K. Kuroda, and C. Kato: *Chem. Lett.* 2057 (1989).
8. K.R. Franklin, E. Lee, and C.C. Nunn: *J. Mater. Chem.* **5**, 565 (1995).
9. M. Meyn, K. Beneke, and G. Lagaly: *Inorg. Chem.* **29**, 5201 (1990).
10. E. Kanezaki, M. Sugiyama, and Y. Ishikawa: *J. Mater. Chem.* **5**, 1969 (1995).
11. E. Kanezaki, T. Sakamoto, A. Ookubo, and K. Ooi: *J. Chem. Soc., Faraday Trans.* **88**, 3583 (1992).
12. MOPAC ver. 5.00 (QCPE No. 455), J.J.P. Steward: *QCPE Bull.* **9**, 10 (1989); T. Hirano: *JCPE Newsletter* **1**, 36 (1989); revised as Ver. 5.01 by J. Toyota for Apple Macintosh.
13. R. Allman: *Chimica* **24**, 99 (1970); *Acta Crystallogr.* **B24**, 972 (1968).
14. A. Streitwieser, Jr.: *Molecular Orbital Theory for Organic Chemists,* Ch. 8, Wiley, New York (1961).
15. D. Briggs and M.P. Seah: *Practical Surface Analysis-Auger and X-Ray Photoelectron Spectroscopy*, Wiley, New York (1982).
16. W.T. Reichie, S.Y. Kang, and D.S. Everhardt: *J. Catal.* **101**, 352 (1986).
17. D.D. Elleman and D. Williams: *J. Chem. Phys.* **25**, 742 (1956).