

# Synthesis and Properties of Terephthalate and Benzoate Intercalates of Mg–Al Layered Double Hydroxides Possessing Varying Layer Charge

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The influence of layer charge on the intercalation of terephthalate and benzoate anions in MgAl layered double hydroxides has been studied. It is found that, under the synthesis conditions used here, incorporation of the anion is dependent upon the Mg:Al ratio of the host sheets. Pure terephthalate and benzoate intercalates are formed for a ratio of 2 or less from both chloride and nitrate solutions. At higher values of layer charge competitive incorporation of the counteranion present in the solution (i.e., chloride or nitrate) occurs with decreased incorporation of organic anions at ratio 3 or higher. Two extreme orientations are observed for the organic anion within the gallery—either vertical (i.e., perpendicular to the layers) or horizontal. In the case of terephthalate a monolayer arrangement exists, whereas for benzoate the vertical arrangement is a bilayer and the horizontal a monolayer. Whether a vertical or horizontal orientation is adopted depends upon the charge on the layers, the temperature, and the degree of hydration of the sample.

## Introduction

Layered double hydroxides (LDHs) consist of positively charged metal hydroxide sheets with anions (along with water) located between the layers to charge compensate. Their use in a variety of applications has recently been reviewed.<sup>1,2</sup> The composition may be generally represented as  $[M(II)_{1-x}M(III)_x(OH)_2]A_{x/n} \cdot mH_2O$ , where M(II) is a divalent cation such as Ni, Mg, Cu, or Zn and M(III) is a trivalent cation such as Al, Cr, Fe, V, or Ga with  $A_{x/n}$  an anion of charge  $n$  such as  $CO_3^{2-}$ ,  $Cl^-$ ,  $SO_4^{2-}$ , or  $NO_3^-$ . A large number of such compounds are known, and an important feature is the relative ease of synthesis of a range of LDH matrixes with significant variation in layer charge (i.e., divalent/trivalent ratio between 1 and 5). In addition an extensive choice of gallery species may be located between the layers.<sup>1</sup>

The anion-exchange properties of these materials have been studied by numerous authors, with the nature of the anion initially present in the starting LDH playing an important role in controlling the ease of exchange.<sup>3</sup> For simple inorganic anions the exchange facility is generally reported to decrease in the order  $NO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-}$ . In general, the more strongly bound anions are those with the smaller radii which result in a decreased spacing between the hydroxide layers.<sup>4</sup> The charge density of the LDH layers also plays a significant role on the anion-exchange properties. The effect of the charge density of MgAl and NiAl LDHs on the anion exchange of carbonate by the decavanadate anion has been reported.<sup>5</sup> The crystal-

linity of the pillared LDHs which result appears to depend on the identity of the starting divalent and trivalent cations within the LDH matrix.<sup>5</sup>

Anion exchange generally requires the exchange to be performed under an inert gas because the competitive incorporation of carbonate from air is a dominant side reaction.<sup>1,2</sup> An alternative way to prepare LDHs with various anions is the coprecipitation of the divalent and trivalent cations in the presence of the anion (the so-called direct-synthesis method). This method has been used to incorporate a variety of organic anions,<sup>6–8</sup> and it was recently applied to prepare pillared LDHs with inorganic anions such as  $\alpha$ -[SiW<sub>11</sub>O<sub>39</sub>] and decavanadate.<sup>9,10</sup>

Our study in this paper concerns the incorporation, by direct synthesis, of organic anions between the layers. In particular, the synthesis is undertaken while systematically varying the Mg:Al ratio, as well as the identity of the starting magnesium and aluminum salts (i.e., nitrate and chloride). We report here specifically on the synthesis of terephthalate and benzoate intercalates of a MgAl LDH where the Mg:Al ratio (i.e., layer charge) has been systematically varied between 1 and 5.

The terephthalate anion was chosen because it has been previously studied at a limited Mg:Al ratio of 2 and 3, and has been used as an important intermediate preswelling agent to incorporate polyoxometallate anions between the layers.<sup>6,11</sup> Given its close molecular

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structure to terephthalate, benzoate was additionally used to study the influence of anion charge on the ease of incorporation as well as orientation in the gallery. The thermal characteristics of these intercalates (using PXRD, thermogravimetry, and evolved gas analysis) are also reported.

## Experimental Section

**Sample Preparation.** The LDHs were prepared by a coprecipitation method similar to that described by Kooli and Jones.<sup>12</sup> As an illustration, 2.24 g (0.056 M) of NaOH was dissolved in 75 cm<sup>3</sup> of deionized water, and 0.028 M of terephthalic acid (C<sub>6</sub>H<sub>4</sub>-1,4-(CO<sub>2</sub>H)<sub>2</sub>, TA) or 6.84 g (0.056 M) of benzoic acid (C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>H, BA) was added to the sodium hydroxide solution. In all preparations the amount of TA or BA within the solutions was double the theoretical value required to balance the positive charge of the layers. To the dissolved organic acid maintained at 55 °C, a solution of Mg and Al salts (nitrate or chloride) with the desired ratio was added dropwise in an air atmosphere. The pH was held constant at 10 by the addition of 2 M sodium hydroxide solution. The slurry obtained was aged at 55 °C for 18 h, filtered, washed with 2 L of boiled deionized water and dried at 60 °C overnight.

The following nomenclature has been used—MgAl<sub>R</sub>X-Y abbreviates as follows: *R* is the ratio of Mg and Al in the synthesis mixture, X is the counterion of the salts used (i.e., nitrate or chloride) and Y is either terephthalate or benzoate, e.g., MgAl<sub>5</sub>NO<sub>3</sub>-TA defines a sample prepared from a solution of Mg and Al nitrate of ratio 5 with terephthalate as the organic anion.

**Characterization Techniques.** Powder X-ray diffraction (PXRD) patterns were obtained using a Philips APD 1700 instrument, with Ni-filtered Cu K $\alpha$  radiation, and a 0.02° step size. The scan times were around 1 h. High-temperature PXRD patterns between room temperature and 270 °C were taken using an Anton Parr heating stage under a nitrogen atmosphere. FTIR spectra were obtained, in the 4000–400 cm<sup>-1</sup> range, using a Nicolet 205 FTIR spectrometer and following the KBr pellet technique; the resolution was 2 cm<sup>-1</sup>, and 100 scans were averaged. Regular scans of pure KBr pellets were taken to ensure the purity of the KBr matrix. Chemical analyses of C, H, and N were obtained using a Carlo Erba Strumentazione Model 1106 elemental analyzer. Chloride content was obtained using the following procedure: 4–6 mg of sample was weighed onto a blank filter paper. This was combusted in an oxygen flask containing 10 mL of deionized water and 0.1 mL of hydrogen peroxide. The flask was then shaken for 15 min in order to absorb all the chloride formed. The contents of the flask were then titrated with 0.005 M silver nitrate using 2,7-bis(2-sulfophenylazo)chromotropeic acid as indicator. The thermogravimetric analysis (TGA) was performed on Polymer Laboratory TGA1500 apparatus coupled to a Leda Mass spectrometer via a quartz transfer line. The TGA was operated at atmospheric pressure and the mass spectrometer had a typical operating pressure of 6 × 10<sup>-7</sup> Torr. The heating rate used for combined TG-MS experiments was 30 °C min<sup>-1</sup>. Differential thermal analysis (DTA) was carried out using a DTA 92 SETRAM apparatus at a heating rate of 5 °C min<sup>-1</sup> in an air atmosphere.

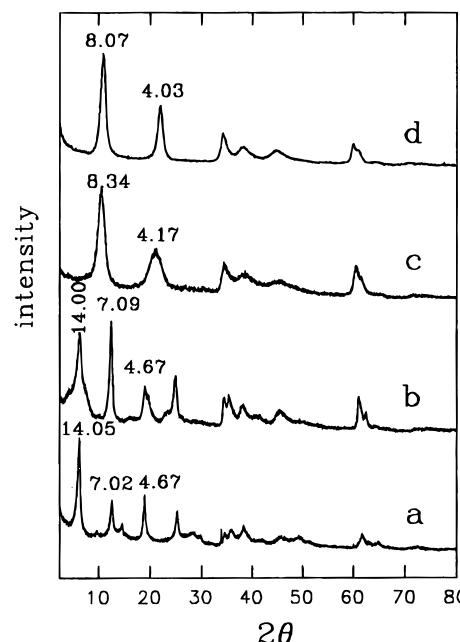
## Results and Discussion

**Synthesis of Intercalates. Terephthalate.** For MgAl<sub>1</sub>NO<sub>3</sub>-TA and MgAl<sub>2</sub>NO<sub>3</sub>-TA, the C, H, and N analysis data (Table 1) indicate similar carbon content with only a trace of nitrogen observed for MgAl<sub>2</sub>NO<sub>3</sub>-TA. For MgAl<sub>3</sub>NO<sub>3</sub>-TA, however, the amount of carbon is significantly reduced and is accompanied by an

**Table 1. Chemical Analysis Data<sup>a</sup>**

| samples                               | C %   | H %  | N %  | Cl % |
|---------------------------------------|-------|------|------|------|
| MgAl <sub>1</sub> NO <sub>3</sub> -TA | 14.22 | 4.09 | nd   |      |
| MgAl <sub>2</sub> NO <sub>3</sub> -TA | 14.58 | 4.28 | 0.18 |      |
| MgAl <sub>3</sub> NO <sub>3</sub> -TA | 4.91  | 3.76 | 2.65 |      |
| MgAl <sub>5</sub> NO <sub>3</sub> -TA | 1.20  | 3.24 | 2.27 |      |
| MgAl <sub>1</sub> Cl-TA               | 14.30 | 4.21 |      | na   |
| MgAl <sub>2</sub> Cl-TA               | 13.08 | 4.28 |      | na   |
| MgAl <sub>3</sub> Cl-TA               | 2.42  | 3.74 |      | 8.9  |
| MgAl <sub>5</sub> Cl-TA               | 0.21  | 3.85 |      | 8.3  |
| MgAl <sub>1</sub> NO <sub>3</sub> -BA | 17.16 | 4.25 |      | na   |
| MgAl <sub>2</sub> NO <sub>3</sub> -BA | 21.22 | 4.50 |      | 0.20 |
| MgAl <sub>3</sub> NO <sub>3</sub> -BA | 4.68  | 3.63 |      | 2.52 |
| MgAl <sub>5</sub> NO <sub>3</sub> -BA | 0.77  | 3.83 |      | 2.56 |
| MgAl <sub>1</sub> Cl-BA               | 18.45 | 4.38 |      | na   |
| MgAl <sub>2</sub> Cl-BA               | 16.12 | 4.24 |      | na   |
| MgAl <sub>3</sub> Cl-BA               | 0.67  | 4.01 |      | 8.34 |

<sup>a</sup> na = not analyzed; nd = analyzed but not detected.



**Figure 1.** PXRD patterns of air-dried TA samples (a) MgAl<sub>1</sub>NO<sub>3</sub>-TA, (b) MgAl<sub>2</sub>NO<sub>3</sub>-TA, (c) MgAl<sub>3</sub>NO<sub>3</sub>-TA, and (d) MgAl<sub>5</sub>NO<sub>3</sub>-TA. In (a) and (b) a vertical orientation of the TA anion is observed. For (c) both TA and NO<sub>3</sub><sup>-</sup> are present and for (d) only NO<sub>3</sub><sup>-</sup> is intercalated.

increase in the nitrogen content suggesting that for ratio 3 both terephthalate and nitrate anions are present in the product. For MgAl<sub>5</sub>NO<sub>3</sub>-TA, a very small carbon content is found, with the amount of nitrogen observed suggesting that NO<sub>3</sub><sup>-</sup> is the main anion in the interlayer region. Similar trends in the relative amounts of organic and inorganic anions are seen when Mg and Al chloride salts are used for the synthesis—see Table 1.

The PXRD patterns for MgAl<sub>1</sub>NO<sub>3</sub>-TA and MgAl<sub>2</sub>NO<sub>3</sub>-TA are shown in Figure 1a,b, respectively. The patterns suggest an expanded structure in both cases with a *d*<sub>003</sub> reflection close to 14.0 Å. Assuming the thickness of the brucite layer is approximately 4.8 Å,<sup>13</sup> the gallery height is close to 9.2 Å. Given that the size of the TA anion is approximately 9.0 Å, this value has previously been ascribed to the presence of the terephthalate anion adopting a vertical arrangement within the gallery.<sup>6,14</sup> Trace 1c shows the PXRD for MgAl<sub>3</sub>NO<sub>3</sub>-TA. For this

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**Table 2. Unit-Cell Parameters and the Corresponding Mg:Al Ratios of the Various LDHs**

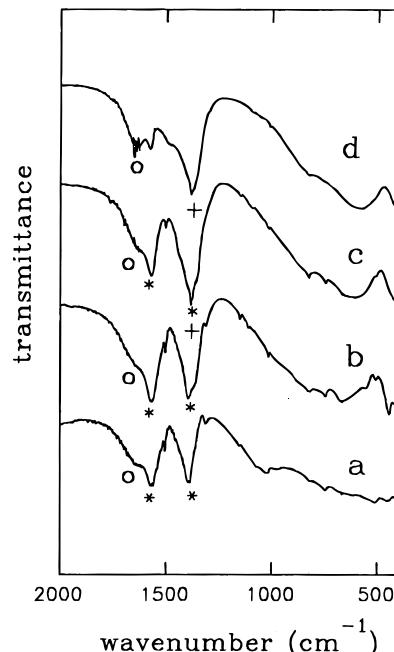
| samples                  | <i>a</i> parameter/<br>Å | <i>c</i> parameter/<br>Å | <i>x</i> =<br>Al/(Mg+Al) | Mg/Al<br>ratio |
|--------------------------|--------------------------|--------------------------|--------------------------|----------------|
| MgAl1NO <sub>3</sub> -TA | 3.01                     | 42.15                    | 0.49                     | 1.03           |
| MgAl2NO <sub>3</sub> -TA | 3.03                     | 42.00                    | 0.39                     | 1.56           |
| MgAl3NO <sub>3</sub> -TA | 3.06                     | 25.02                    | 0.25                     | 2.92           |
| MgAl5NO <sub>3</sub> -TA | 3.09                     | 24.21                    | 0.18                     | 4.55           |
| MgAl1Cl-TA               | 3.01                     | 42.33                    | 0.50                     | 1.03           |
| MgAl2Cl-TA               | 3.04                     | 43.04                    | 0.33                     | 2.00           |
| MgAl3Cl-TA               | 3.07                     | 24.04                    | 0.24                     | 3.16           |
| MgAl5Cl-TA               | 3.08                     | 24.80                    | 0.18                     | 4.56           |
| MgAl1NO <sub>3</sub> -BA | 3.01                     | 45.69                    | 0.48                     | 1.03           |
| MgAl2NO <sub>3</sub> -BA | 3.02                     | 45.78                    | 0.43                     | 1.32           |
| MgAl3NO <sub>3</sub> -BA | 3.05                     | 24.90                    | 0.26                     | 2.77           |
| MgAl5NO <sub>3</sub> -BA | 3.09                     | 24.06                    | 0.18                     | 4.55           |
| MgAl1Cl-BA               | 3.01                     | 47.01                    | 0.47                     | 1.03           |
| MgAl2CBA                 | 3.04                     | 23.63                    | 0.35                     | 2.00           |
| MgAl3Cl-BA               | 3.07                     | 23.58                    | 0.23                     | 3.16           |

material an expanded structure is not obtained and instead two broad peaks are present at 8.34 and 4.17 Å which we assign as  $d_{003}$  and  $d_{006}$  of a phase with TA and  $\text{NO}_3^-$  both present in the interlayer.  $\text{NO}_3^-$  is the predominant anion present with the TA anion adopting an orientation parallel to the layers. (That TA is present between the layers and not simply physisorbed on the external surfaces of the particles is confirmed by hydration experiments; see later.) For MgAl5NO<sub>3</sub>-TA, intercalation of terephthalate does not occur, and nitrate anions are incorporated between the layers (Figure 1d), with the PXRD pattern similar to that of a pure nitrate containing LDH.<sup>1</sup> Similar trends are seen for chloride preparations. For MgAlCl1-TA and MgAlCl2-TA terephthalate is present in a vertical orientation. For MgAl3Cl-TA, however, the PXRD pattern (not shown) consists of two sharp reflections at 8.03 and 4 Å, similar to that expected for a pure chloride LDH.<sup>15</sup>

On the basis of PXRD and chemical analysis, therefore, we conclude that at ratio 3 little organic anion is incorporated, although slightly more is present for the nitrate preparation as compared to the chloride. As reported, below, however, these small differences appear to have an effect on the swelling properties of the materials and the ability of the organic component to adopt a vertical orientation.

Table 2 presents the Mg:Al ratios for the various LDHs as determined by PXRD. To obtain these values we have used the  $d_{110}$  position in the PXRD pattern and the relationship  $a = 2d_{110}$ .<sup>16</sup> The decrease in the *a* parameter as aluminum content increases is the result of the smaller ionic radius of  $\text{Al}^{3+}$  (0.50 Å) compared to  $\text{Mg}^{2+}$  (0.65 Å).<sup>17,18</sup> This method of determining the Mg:Al ratio in the layers is well established as a reliable method for determining such ratios.<sup>1,16</sup> Alternative methods (e.g., chemical analysis or X-ray fluorescence) suffer from the possibility of erroneous values as a result of precipitation of  $\text{Mg}(\text{OH})_2$  and/or  $\text{Al}(\text{OH})_3$  phases upon the LDH surfaces which are possibly amorphous and therefore not detected by PXRD.

For MgAl1NO<sub>3</sub>-TA the resulting Mg:Al ratio within the LDH is close to the theoretical value, i.e., the Mg:Al ratio in the starting solution is reflected in the value



**Figure 2.** FT-IR spectra of terephthalate samples (a) MgAl1NO<sub>3</sub>-TA, (b) MgAl2NO<sub>3</sub>-TA, (c) MgAl3NO<sub>3</sub>-TA, and (d) MgAl5NO<sub>3</sub>-TA. (\*) Terephthalate, (○) water, and (+) nitrate bands. Spectrum (c) suggests the co-intercalation of TA and  $\text{NO}_3^-$  anions.

obtained in the precipitation product. For an Mg:Al ratio in the starting solutions greater than 1, the values obtained in the product are lower than those of the corresponding solutions, suggesting that there is incomplete precipitation of magnesium.<sup>2</sup>

The FTIR spectra of the LDHs obtained with terephthalate for different values of the Mg:Al ratio have been recorded. A broad absorption band between 3600 and 3200  $\text{cm}^{-1}$  is associated with the stretching mode of hydrogen-bonded hydroxyl groups from both the hydroxide layers and interlayer water.<sup>19</sup> A water deformation band is recorded at 1650  $\text{cm}^{-1}$ . Of particular interest is the region between approximately 1600 and 1300  $\text{cm}^{-1}$  (see Figure 2). For MgAl1NO<sub>3</sub>-TA and MgAl2NO<sub>3</sub>-TA two main bands corresponding to terephthalate<sup>20,21</sup> are present at 1567 and 1390  $\text{cm}^{-1}$  (Figure 2a,b). These two bands are also present for MgAl3NO<sub>3</sub>-TA (Figure 2c) although with decreased intensity. Additionally, for MgAl3NO<sub>3</sub>-TA there is an absorption at 1380  $\text{cm}^{-1}$ , which we associate with the presence of the nitrate anions.<sup>22</sup> Indeed, the FTIR spectrum of MgAl5NO<sub>3</sub>-TA (Figure 2d) shows a strong absorption at 1380  $\text{cm}^{-1}$  corresponding to nitrate and only weak bands for terephthalate. Again similar trends are seen for chloride preparations.

**Benzoate.** The carbon content (Table 1) indicates that benzoate is the main charge-balancing anion for MgAl1NO<sub>3</sub>-BA and MgAl2NO<sub>3</sub>-BA with little or no nitrogen analyzed. For MgAl3NO<sub>3</sub>-BA, however, the carbon content decreases. This decrease is accompanied by an

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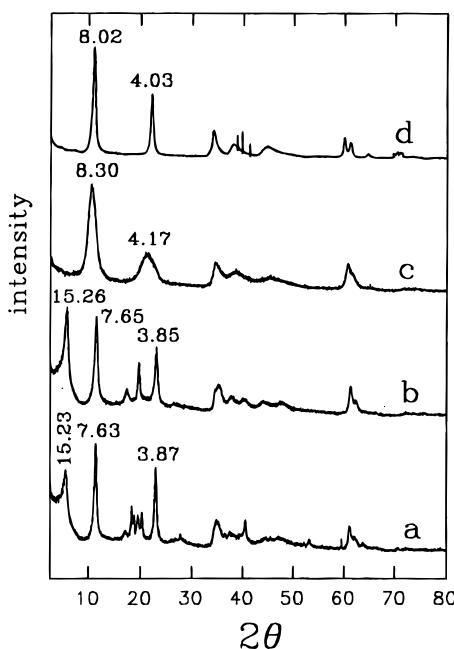
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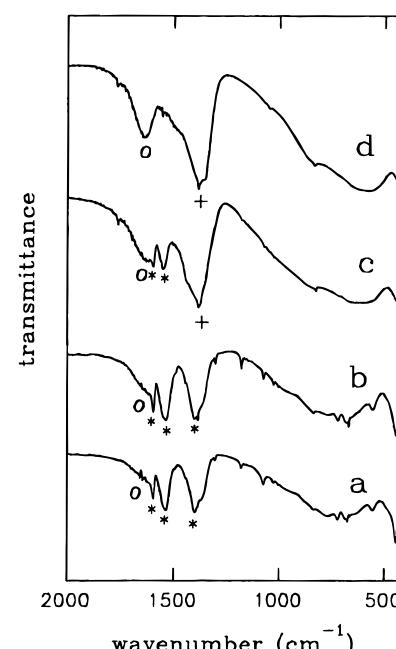


**Figure 3.** PXRD patterns of samples (a)  $\text{MgAl1NO}_3\text{-BA}$ , (b)  $\text{MgAl2NO}_3\text{-BA}$ , (c)  $\text{MgAl3NO}_3\text{-BA}$ , and (d)  $\text{MgAl5NO}_3\text{-BA}$ . At R(1) and R(2) an expanded bilayer structure is formed, while for R(3) a horizontal monolayer of benzoate and nitrate coexists. At R(5) only nitrate is incorporated.

increase in the percentage of nitrate present suggesting the presence of both benzoate and nitrate for this sample. For  $\text{MgAl5NO}_3\text{-BA}$  chemical analysis indicates  $\text{NO}_3^-$  is the predominant anion present. For chloride solutions and for ratio 1 and 2 similar trends are seen to those for nitrate. For  $\text{MgAl3Cl-BA}$  the amount of chloride increases and the carbon content is significantly decreased. For  $\text{MgAl5Cl-BA}$  the analysis suggests only  $\text{Cl}^-$  incorporation. In a similar way to that for terephthalate, the values of the Mg:Al ratio in the benzoate samples are, except for  $\text{MgAl1NO}_3\text{-BA}$ , lower than those expected from the starting solutions (Table 2).

The PXRD patterns of samples  $\text{MgAl1NO}_3\text{-BA}$  and  $\text{MgAl2NO}_3\text{-BA}$  are similar. In each case a well-ordered and expanded intercalate with a  $d_{003}$  of approximately of 15.2 Å is produced; see Figure 3a,b. This value of  $d_{003}$  corresponds to a gallery height of 10.4 Å and agrees with previous values reported for benzoate-intercalated materials.<sup>8,14,23</sup> Given that the length of the benzoate anion is approximately 7 Å,<sup>14</sup> such a value is generally associated with the formation of a bilayer-like structure within the gallery. In this arrangement the carboxyl groups are linked by hydrogen bonding to the hydroxide sheets and the aromatic groups located within the center of the gallery. The overall result is a hydrophobic membrane-like region, similar to that reported for fatty acids.<sup>24</sup>

For  $\text{MgAl3NO}_3\text{-BA}$ , the PXRD pattern (Figure 3c) indicates that a similarly expanded structure is not formed. The broad peaks at 8.30 and 4.17 Å are interpreted (on the basis of the chemical analysis data and FTIR (see below)) as resulting from the presence of both benzoate anions (in a horizontal arrangement) and nitrate anions between the layers. Precipitation



**Figure 4.** FT-IR spectra of benzoate samples (a)  $\text{MgAl1NO}_3\text{-BA}$ , (b)  $\text{MgAl2NO}_3\text{-BA}$ , (c)  $\text{MgAl3NO}_3\text{-BA}$ , and (d)  $\text{MgAl5NO}_3\text{-BA}$ . (\*) Benzoate, (○) water, and (+) nitrate bands. In spectrum (c) peaks for both BA and  $\text{NO}_3^-$  are present.

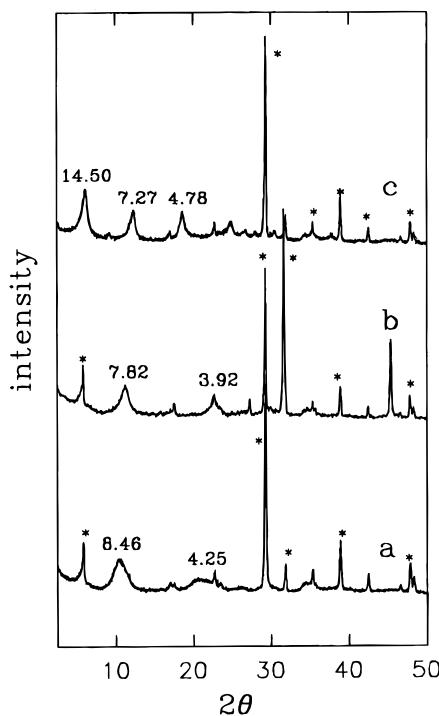
from a solution with a Mg:Al ratio of 5 yields a PXRD pattern (Figure 3d) which consists of relatively sharp reflections with a  $d_{003}$  close to 8.02 Å which, as suggested by the chemical analysis, we interpret as due to the presence of predominantly nitrate anions in the gallery region. For chloride solutions, the PXRD patterns for  $\text{MgAl1Cl-BA}$  consists of a  $d_{003}$  reflection at 15.7 Å, similar to  $\text{MgAl1NO}_3\text{-BA}$ . For  $\text{MgAl2Cl-BA}$  a broad line is present at approximately 5° (2θ), close to the position of the  $d_{003}$  reflections observed for  $\text{MgAl1Cl-BA}$  with the first sharp peak at 11° (2θ) corresponding to 7.89 Å. Since the carbon content is relatively high for this sample, it is possible that this value is associated with benzoate anions parallel to the hydroxide layers<sup>12</sup> (and is to be compared with the vertical orientation obtained using nitrate salts at the same ratio). The broad peak at 5° (2θ) may indicate that vertical incorporation occurs but that there is a greater degree of disorder of the bilayer arrangement of BA anions in the gallery region for this sample than for  $\text{MgAl2NO}_3\text{-BA}$ . For  $\text{MgAl3Cl-BA}$  and  $\text{MgAl5Cl-BA}$  the pattern is similar to that for a MgAl chloride LDH phase in agreement with chemical analysis and suggesting that very little, if any, intercalation of organic anion occurs.

The FTIR spectra support the analytical and PXRD data (Figure 4). The presence and intensity of the characteristic carboxyl and phenyl bands at 1588, 1532, and 1395  $\text{cm}^{-1}$  which are associated with benzoate<sup>21</sup> are directly related to the Mg:Al ratio. The bands are clearly present for  $\text{MgAl1NO}_3\text{-BA}$  and  $\text{MgAl2NO}_3\text{-BA}$  while for  $\text{MgAl3NO}_3\text{-BA}$  there is an additional absorption at 1380  $\text{cm}^{-1}$  corresponding to the co-intercalated nitrate. For  $\text{MgAl5NO}_3\text{-BA}$  the FTIR spectrum is characteristic of a MgAl nitrate LDH, confirming that little intercalation of benzoate occurs.

**Nature of the LDH Initially Produced in the Gel Phase.** Clearly, therefore, the feasibility of intercalating terephthalate or benzoate is related to both the charge on the layers and to some extent on the identity

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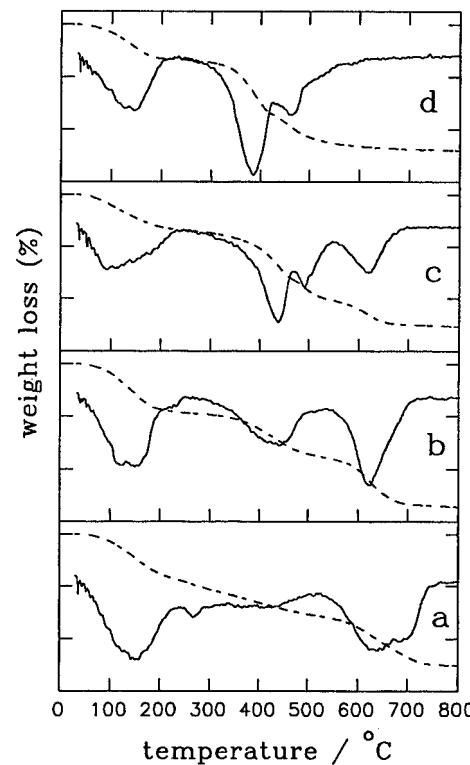
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**Figure 5.** PXRD patterns of benzoate samples prepared with a Mg:Al ratio 2 from different salt solutions. The patterns were obtained after the complete mixing of salt and sodium hydroxide but before hydrothermal treatment: (a) nitrate and (b) chloride. Trace (c) corresponds to a sample prepared with terephthalate as the anion from a nitrate solution. (\*) Sodium salts and sodium benzoate.

of the inorganic counteranion present in the starting solutions. To probe this point further, we have looked at the nature of the gels which are initially precipitated in the reaction mixture, i.e., before any aging.

Figure 5a,b shows the PXRD patterns for a benzoate LDH mixture with a Mg:Al ratio of 2 directly after precipitation using nitrate and chloride starting salts. For both samples the initial traces correspond to the inorganic intercalates (i.e., nitrate or chloride LDHs) with  $d_{003}$  values at 8.46 and 7.82 Å, respectively. The sharp peaks present in the patterns correspond to sodium nitrate or chloride as well as precipitated sodium benzoate. We conclude that the incorporation of the benzoate anion does not occur directly during precipitation but takes place later, most likely during the hydrothermal treatment at 55 °C. As a result, the incorporation of the organic anion will be determined by the ease of displacement of the nitrate or chloride anions.<sup>3</sup> With terephthalate (Figure 5c), the mechanism appears to be different. Coprecipitation leads to the formation of a MgAl LDH with terephthalate anions rapidly incorporated irrespective of whether nitrate or chloride salts solutions are used. The PXRD patterns show a LDH phase with a  $d_{003}$  of 14.5 Å, corresponding to a LDH with terephthalate oriented vertically between the layers. Additional reflections of the sodium salts are also observed. The nitrate or chloride anions are either rapidly exchanged by the divalent terephthalate



**Figure 6.** TGA (---) and (—) derivative curves of LDH samples (a)  $\text{MgAl1NO}_3\text{-TA}$ , (b)  $\text{MgAl2NO}_3\text{-TA}$ , (c)  $\text{MgAl3NO}_3\text{-TA}$ , and (d)  $\text{MgAl5NO}_3\text{-TA}$ . Three general regions are noted: room temperature to 270 °C; 300–470 °C; >500 °C (see text).

or terephthalate is incorporated directly upon precipitation. The time scale of the PXRD experiment made here not allowing us to distinguish between these possibilities.

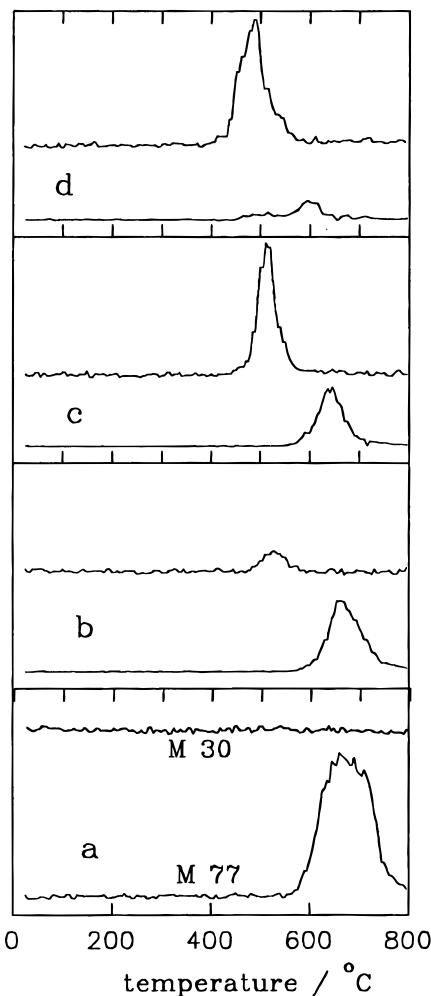
## Physical Properties

**Thermal Characteristics.** The TGA traces for  $\text{MgAl1NO}_3\text{-TA}$ ,  $\text{MgAl2NO}_3\text{-TA}$ ,  $\text{MgAl3NO}_3\text{-TA}$ , and  $\text{MgAl5NO}_3\text{-TA}$  (Figure 6) indicate three general regions of mass loss. The first, corresponding to the removal of physisorbed and interlayer water, is present for all samples and extends from room temperature to approximately 270 °C.<sup>25</sup> The second follows the dehydroxylation of the lattice in the 300–470 °C range. In the case of Mg:Al ratios 3 and 5 this is also accompanied by loss of nitrate anions.<sup>3</sup> The third loss, above 500 °C, corresponds to the elimination and combustion of the terephthalate anion and is significant only for the ratio 1 and 2 samples.<sup>20</sup> The first two weight loss steps are also monitored by DTA (not shown) as two endothermic peaks with minima at 130 and 400 °C with an exothermic peak (maximum at 560 °C) corresponding to the combustion of the organic anion. Qualitatively, the temperature of this exothermic peak shifts to lower temperatures as the Mg:Al ratio increases from 1 to 3 as a result of the decrease in the electrostatic interaction between the layer and the terephthalate.<sup>26</sup> This analysis of the TGA and DTA data is confirmed by mass spectral analysis of the evolved gases during heating (Figure 7). Associated with  $\text{MgAl1NO}_3\text{-TA}$  and  $\text{MgAl2NO}_3\text{-TA}$ , the loss of terephthalate at ca. 650 °C (detected as  $\text{C}_6\text{H}_5^+$  at  $m/z = 77$ <sup>27</sup>) is observed, while water and nitrate decomposition are seen at lower temperature.

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**Figure 7.** TG/MS spectra obtained for samples described in Figure 6. M 77 and M 30 correspond to  $C_6H_5^+$  and  $NO^+$  species, respectively. The signal intensity at M 77 (for TA decomposition) decreases as the Mg:Al ratio increases and is accompanied by an increase in the M 30 ( $NO_3^-$ ) peak.

For  $MgAl1NO_3$ -BA and  $MgAl2NO_3$ -BA, the TGA curves indicate three steps, similar to the terephthalate samples. For  $MgAl5NO_3$ -BA, the step due to the loss of the benzoate is not observed (and is very small for  $MgAl3NO_3$ -BA). Two weight loss regions are recorded at lower temperature corresponding to loss of water and to dehydroxylation (along with anion decomposition for ratio 3 and above). These are monitored in the DTA by endothermic peaks with minima at 170 and 350 °C, respectively. Analysis of the evolved gases supports the interpretation of the TGA and DTA data. For  $MgAl1NO_3$ -BA and  $MgAl2NO_3$ -BA, there is a weight loss centered at 575 °C with an associated signal at  $m/z = 77$ . Little nitrate evolution ( $m/z = 30$ ,  $NO^+$ ) occurs for these two samples. For  $MgAl3NO_3$ -BA, only a small signal at mass 77 is observed, with nitrate clearly evolved. In the case of  $MgAl5NO_3$ -BA, the mass 77 signal is completely absent, and for this sample a profile similar to that expected for nitrate intercalated LDH is produced.

The TG and DTA curves for the chloride samples follow the pattern established for the nitrate. For  $MgAl1Cl$ -TA and  $MgAl2Cl$ -TA the curves are dominated by three regions, whereas for  $MgAl3Cl$ -TA and  $MgAl5Cl$ -TA there are principally two, corresponding to the loss of intercalated water and dehydroxylation accompanied

**Table 3. Chemical Formulas for the LDHs**

| samples         | chemical formulas  |
|-----------------|--|
| $MgAl1NO_3$ -TA | $Mg_{0.51}Al_{0.49}(OH)_2(TA)_{0.25}\cdot 0.81H_2O$              |
| $MgAl2NO_3$ -TA | $Mg_{0.61}Al_{0.39}(OH)_2(TA)_{0.195}\cdot 1.16H_2O$             |
| $MgAl3NO_3$ -TA | $Mg_{0.75}Al_{0.25}(OH)_2(TA)_{0.03}(NO_3)_{0.20}\cdot 0.7H_2O$  |
| $MgAl5NO_3$ -TA | $Mg_{0.82}Al_{0.18}(OH)_2(NO_3)_{0.18}\cdot 0.6H_2O$             |
| $MgAl1Cl$ -TA   | $Mg_{0.51}Al_{0.49}(OH)_2(TA)_{0.25}\cdot 0.83H_2O$              |
| $MgAl2Cl$ -TA   | $Mg_{0.67}Al_{0.33}(OH)_2(TA)_{0.17}\cdot 1.0H_2O$               |
| $MgAl3Cl$ -TA   | $Mg_{0.76}Al_{0.24}(OH)_2(Cl)_{0.19}(TA)_{0.03}\cdot 0.53H_2O$   |
| $MgAl5Cl$ -TA   | $Mg_{0.82}Al_{0.18}(OH)_2(Cl)_{0.18}\cdot 0.60H_2O$              |
| $MgAl1NO_3$ -BA | $Mg_{0.52}Al_{0.48}(OH)_2(BA)_{0.48}\cdot 1.20H_2O$              |
| $MgAl2NO_3$ -BA | $Mg_{0.57}Al_{0.43}(OH)_2(BA)_{0.43}\cdot 1.08H_2O$              |
| $MgAl3NO_3$ -BA | $Mg_{0.74}Al_{0.27}(OH)_2(BA)_{0.13}(NO_3)_{0.13}\cdot 0.57H_2O$ |
| $MgAl5NO_3$ -BA | $Mg_{0.82}Al_{0.18}(OH)_2(NO_3)_{0.18}\cdot 0.6H_2O$             |
| $MgAl1Cl$ -BA   | $Mg_{0.54}Al_{0.46}(OH)_2(BA)_{0.47}\cdot 1.13H_2O$              |
| $MgAl2Cl$ -BA   | $Mg_{0.65}Al_{0.35}(OH)_2(BA)_{0.35}\cdot 0.8H_2O$               |
| $MgAl3Cl$ -BA   | $Mg_{0.77}Al_{0.23}(OH)_2(Cl)_{0.23}\cdot 0.62H_2O$              |

by the removal of the chloride anion.<sup>3</sup> In the case of  $MgAl3Cl$ -TA, only a small loss of terephthalate is detected.

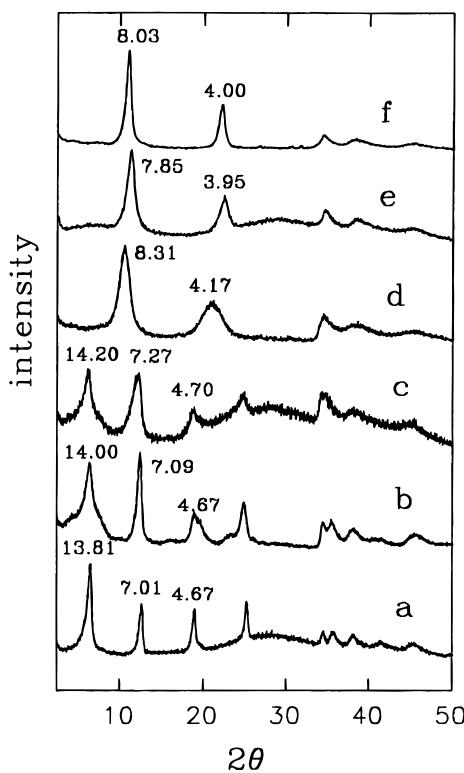
For the samples  $MgAl1Cl$ -BA,  $MgAl2Cl$ -BA, and  $MgAl5Cl$ -BA, TG and DTA curves are also comparable to those obtained from nitrate salts at the same ratios. However, for  $MgAl3Cl$ -BA the TG is different from that of  $MgAl3NO_3$ -BA; only two general stages are observed, corresponding to the loss of intercalated water, and to dehydroxylation accompanied by the removal of chloride as  $HCl$  gas.<sup>28</sup> DTA shows two endothermic peaks. No weight loss related to the elimination of the organic anion is observed, which confirms that the incorporation of organic anions is significantly reduced in these LDHs. Table 3 shows the formulas calculated for the various compounds based upon the chemical analysis data in Tables 1 and 2 as well as the associated weight losses.

#### Effect of Water Content on Orientation of Guest.

For terephthalate samples prepared at Mg:Al ratios 1 and 2 and irrespective of the identity of the salt solutions, the PXRD patterns indicate that the anion is vertically oriented in the layers before and after drying of the samples (Figure 8a,b). For  $MgAl3NO_3$ -TA a vertical arrangement is obtained before drying ( $d_{003}$  of ca. 14.2 Å). After removing the excess water, however, this structure is unstable and collapses—as shown by the shift of  $d_{003}$  from 14.2 to 8.34 Å (Figure 8c,d), i.e., a change from a vertical to horizontal arrangement. Dispersing the  $MgAl3NO_3$ -TA again for 3 h in deionized water results in the regeneration of an expanded phase with a  $d_{003}$  of 14.10 Å. The process is completely reversible, and when the sample is further dried, the structure again collapses. With  $MgAl5NO_3$ -TA, an expanded structure is not observed for a wet sample, further confirming that TA is not incorporated at this ratio.

The results for  $MgAl1Cl$ -TA and  $MgAl2Cl$ -TA are similar to those for  $MgAl1NO_3$ -TA and  $MgAl2NO_3$ -TA with no difference in the PXRD patterns before and after drying the samples. For both samples the anion remains in a vertical orientation between the layers. For  $MgAl3Cl$ -TA (Figure 8e,f) and  $MgAl5Cl$ -TA the observed  $d_{003}$  is close to 8 Å in both the wet and dry state. Although nitrate and chloride appear to be the principal anions in the interlayer at ratio 3 the possibility of the TA adopting a vertical orientation differs between  $Cl^-$  and  $NO_3^-$ , with the nitrate system amenable to a vertical arrangement for a heavily hydrated sample.

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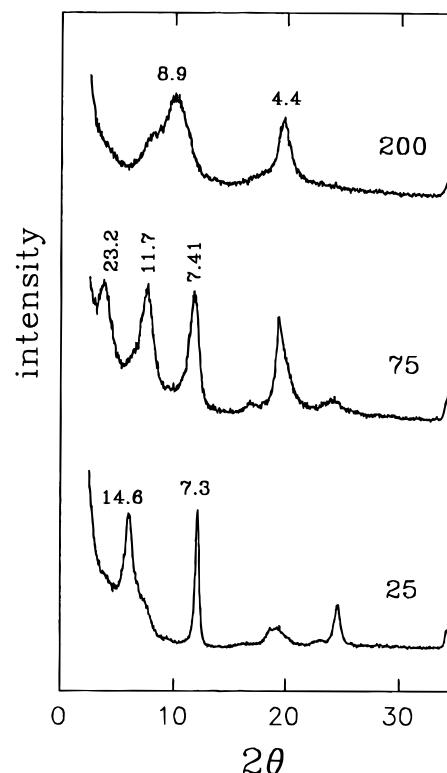
**Figure 8.** PXRD patterns of (a, b)  $\text{MgAl}_2\text{NO}_3\text{-TA}$ , (c, d)  $\text{MgAl}_3\text{NO}_3\text{-TA}$ , and (e, f)  $\text{MgAl}_3\text{Cl}\text{-TA}$ , before and after drying; (a, b) shows an expanded structure in both the wet and dry state. In the case of (c, d) from nitrate a transition between an expanded and collapsed phase is seen. For (e, f) from chloride an expanded phase does not occur for the wet or dry sample.

For  $\text{MgAl}_1\text{NO}_3\text{BA}$  and  $\text{MgAl}_2\text{NO}_3\text{BA}$ , no difference is observed when the PXRD patterns are recorded before and after drying of the samples and under both conditions a bilayer arrangement is observed with a  $d_{003}$  of approximately 15.2 Å. For  $\text{MgAl}_3\text{NO}_3\text{BA}$  where the benzoate anions are, for a dry sample, in a horizontal arrangement, the PXRD pattern does not change following exposure to water, with the anions remaining in a horizontal arrangement.

In the case of  $\text{MgAl}_2\text{Cl-BA}$ , while before drying the PXRD pattern indicated that the layer structure is expanded with a  $d_{003}$  of about 15.7 Å, after drying this expanded structure collapses ( $d_{003}$  approximately 7.80 Å).

**Variation of Anion Orientation with Temperature.** For  $\text{MgAl}_1\text{NO}_3\text{-TA}$  and  $\text{MgAl}_1\text{Cl-TA}$  in which the TA is vertically oriented the position of the 003 reflection is essentially constant up to 270 °C, although there is some decrease in the intensities of other reflections which may be the result of disorder or loss of interlayer water.

For  $\text{MgAl}_2\text{NO}_3\text{-TA}$  and  $\text{MgAl}_2\text{Cl-TA}$  the terephthalate anion is initially in a vertical orientation between the layers, but above 150 °C (at a temperature where water loss becomes important) the expanded structure collapses, with a shift in the position of the (003) reflection from 14.6 to 8.9 Å suggesting a horizontal arrangement for the anion (Figure 9). At intermediate temperatures, e.g., at 75 °C, reflections at 23.2, 11.7, and 7.41 Å are observed. The value of 23.2 Å has been rationalized in terms of an ordered interstratification of collapsed and expanded layers,<sup>29</sup> with  $d$  value of the



**Figure 9.** Temperature dependence of the PXRD patterns for  $\text{MgAl}_2\text{NO}_3\text{-TA}$  after heat treatment at different temperatures (°C). The reflection at 23.2 Å is associated with the creation of an interstratified arrangement of vertical and horizontal terephthalate anions.

003 peak close to the sum of the  $d_{003}$  of the vertical orientation structure at room temperature and the  $d_{003}$  of the horizontal arrangement at 150 °C (Scheme 1). Also discussed in ref 29 is the influence of charge density of the layers with respect to the size of the incorporated anions.

The cooling to room temperature under a flow of dry nitrogen of a sample previously heated to 270 °C indicates that the horizontal orientation is retained (Figure 10a), although contact of the sample to moist air leads, after 2 h, to a shift in the  $d_{003}$  reflection from 8.37 back to 14.50 Å and the recovery of the vertical arrangement (Figure 10c). At intermediate times (about 15 min) in moist air, the interstratified structure of 22.6 Å is created (Figure 10b). Thus it appears that the rehydration of the collapsed structure also occurs via an alternating structure of collapsed and expanded layers.

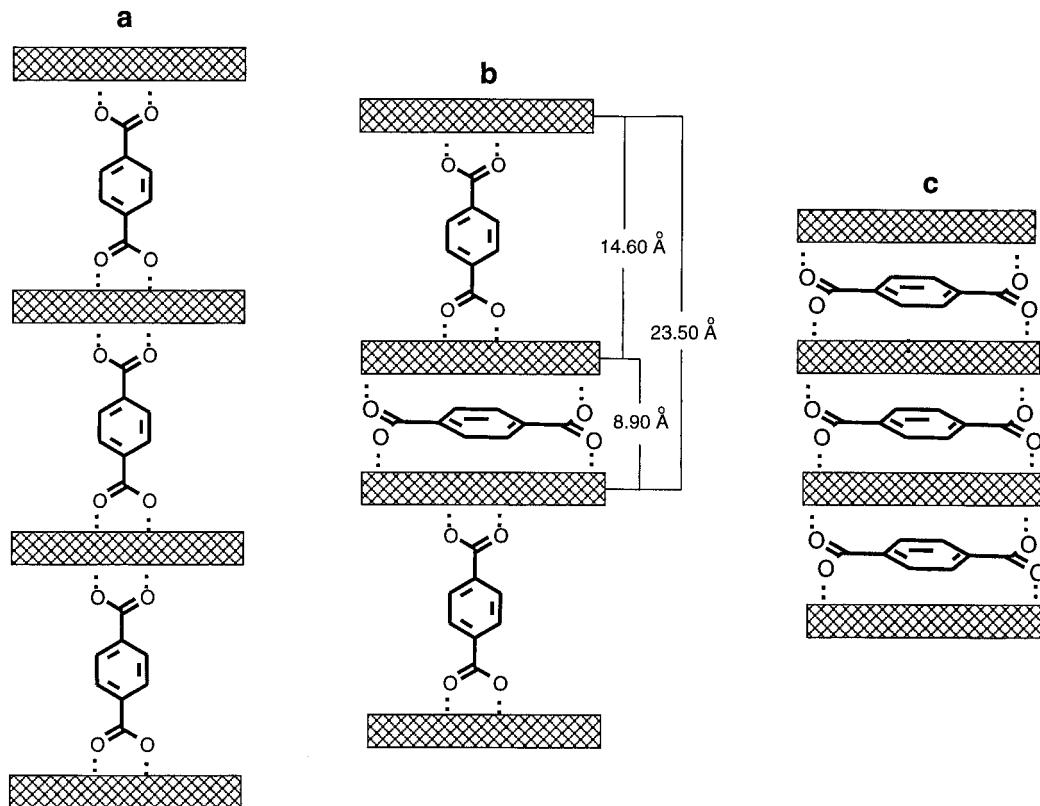
For  $\text{MgAl}_3\text{NO}_3\text{-TA}$ , in which the TA is initially oriented parallel to the layers, as expected no change is observed in the  $d_{003}$  value upon heating to 260 °C, although the intensity of the 006 reflection (at ca. 4 Å) decreases. It has been reported that the intensities of the 001 reflections are related to the interlayer water content between the layer,<sup>30</sup> and the removal of interlayer water induces disorder in the layer stacking sequence, perhaps due to concomitant partial dehydroxylation of the layers.<sup>31</sup> When the sample is rehydrated in air the intensity of the 006 reflection also increases.

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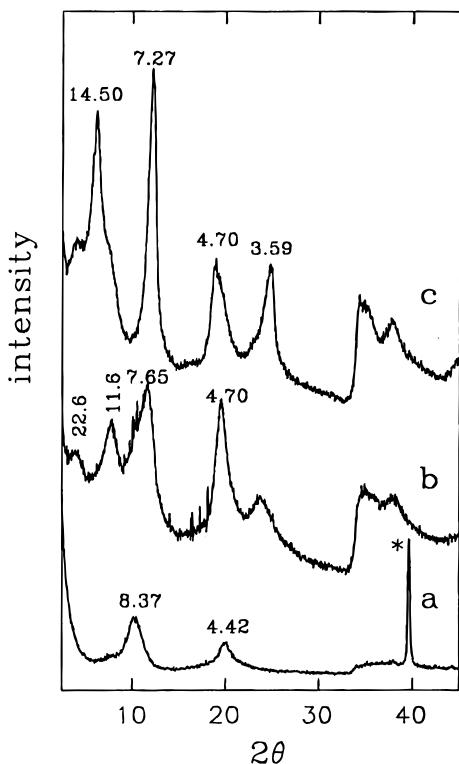
(31) Brindley, G. W.; Kikkawa, S. *Clays Clay Miner.* **1980**, 28, 87.

**Scheme 1. Proposed Model for Structural Changes Occurring during the Heat Treatment and Loss of the Interlayer Water of  $\text{MgAl}_2\text{NO}_3$ -TA Sample at (a) 25, (b) 100, and (c) 200 °C**

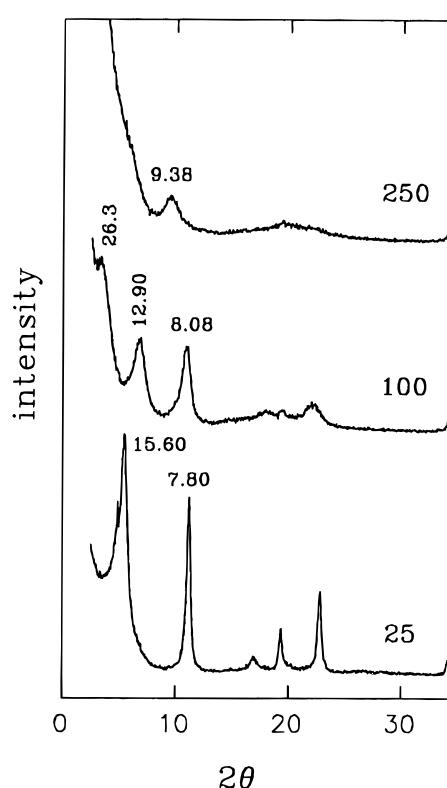


The variation with temperature of PXRD patterns of the benzoate samples  $\text{MgAl}_1\text{NO}_3$ -BA and  $\text{MgAl}_1\text{Cl}$ -BA indicate that the bilayer structure is stable up to 200 °C. At temperatures higher than 250 °C the structure

collapses, and the value falls to ca. 8.25 Å, suggesting the creation of a monolayer between the sheets. For  $\text{MgAl}_2\text{NO}_3$ -BA, the PXRD patterns (Figure 11) show that between 50 and 100 °C, a new phase is observed,



**Figure 10.** PXRD of a sample  $\text{MgAl}_2\text{NO}_3$ -TA previously treated at 270 °C and then cooled (a) in dry nitrogen atmosphere and in moist air for (b) 15 min and (c) 2 h. Rehydration occurs via an interstratified arrangement. Asterisk: from sample holder.



**Figure 11.** Temperature dependence of PXRD patterns of  $\text{MgAl}_2\text{NO}_3$ -BA after heat treatment at different temperatures (at (a) 25, (b) 100, and (c) 250 °C). An interstratified structure is indicated by the peak at 26.3 Å.

with 003, 006, and 009 reflections at 26.3, 12.90, and 8.08 Å, respectively. This change in the PXRD patterns suggests that a similar mechanism to that for the TA intercalates is taking place with the formation of an interstratified compound consisting of alternate layers containing vertical (15.6 Å) and horizontal (9.38 Å) benzoate anions. At higher temperatures this superstructure is lost, and a new  $d_{003}$  reflection at 9.38 Å is obtained, corresponding to a collapsed monolayer formation. The  $d_{003}$  value of 9.38 Å is higher than the value obtained at 250 °C in the case of MgAl1NO3-BA ( $d_{003} = 8.25$  Å) and might be related to the electrostatic interaction between the anion and the hydroxide layers or that the benzoate anions are tilted slightly with respect to the layers. Cooling these samples in moist air does not result in any change in the PXRD pattern, the benzoate anion remaining in a horizontal arrangement and reexpansion is not possible. For MgAl2Cl-BA, in which the benzoate anions is believed to lie parallel to the layers, no significant change at higher temperature is observed.

### Concluding Remarks

Independent of the identity of the organic anion, the general trend concerning the Mg:Al ratios in the LDHs is that the experimental Mg:Al ratios are lower using nitrate salts than with chloride. The use of organic MgAl LDHs as an intermediate phase to introduce larger oxometallate anions between the layers has been reported.<sup>6,11,20</sup> The incorporation and orientation of terephthalate and benzoate anions between the hydroxide layers have been found to be related to the Mg:Al ratios (i.e., the charge density) of the layers, and to the degree of hydration. It is likely, therefore, to limit the Mg:Al ratios for which this "preexpansion" procedure will be useful.

The thermal stability of LDHs containing large inorganic anions has previously been described.<sup>32-34</sup> Few studies have been reported concerning organic anions.<sup>8,29</sup> The thermal stability of the terephthalate intercalates depends also on the Mg:Al ratios. The expanded structure is stable up to 270 °C for Mg:Al ratio 1, and a vertical orientation is preserved. During the loss of interlayer water, for Mg:Al ratio 2, the expanded structure collapses, and a horizontal arrangement is preferred beyond 150 °C. A partial collapse of the layers, resulting in ordered interstratification of collapsed and expanded layers, is observed at approximately 75 °C. The expanded structure is regenerated after rehydration via an interstratified structure. For benzoate, and for a sample with Mg:Al ratio close to 1, the bilayer structure is stable until 200 °C and collapses at 270 °C. At Mg:Al ratio 2 an interstratified material is also obtained, collapsing at high temperatures. However, the rehydration of the samples indicates that the benzoate anion remains in a horizontal orientation once collapse has taken place.

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