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Selective Ion-Exchange Intercalation of Isomeric Dicarboxylate Anions into the Layered Double Hydroxide $[LiAl_2(OH)_6]Cl\cdot H_2O$

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The dicarboxylate anions 1,4-benzenedicarboxylate and fumarate can be selectively intercalated into the layered double hydroxide $[LiAl_2(OH)_6]Cl\cdot H_2O$ from equimolar molar mixtures of the 1,2-, 1,3-, and 1,4-benzenedicarboxylate and fumarate and maleate isomers, respectively. Time-resolved in situ energy-dispersive X-ray diffraction studies have shown that these are the thermodynamic products following the conversion of an initial phase in which all the anions are simultaneously intercalated.

Introduction

Intercalation of inorganic or organic ions into lamellar inorganic lattices is a widely studied reaction.[1−3] It provides synthetic chemists with a low-temperature route to modify both the structural characteristics and the reactivity of inorganic solids in a subtle and controllable manner.[4,5] Selective intercalation reactions have been reported previously for several layered systems including metal phosphonates,[6,7] magnesium aluminum oxide,[8] and montmorillonite.[9] In the restructuring of magnesium aluminum oxide to the layered double hydroxide in the presence of benzenecarboxylate anions the selectivity was governed by the electronic charge and aluminum content of the layered double hydroxide. It was found that the selectivity for the anions with higher charge increased with increasing aluminum content. Shape and carbon number selectivity of amines and alcohols has been shown for the metal phosphonates $VO(O_3PR)\cdot H_2O$ and $M(O_3PCH_3)\cdot H_2O$ ($M = Mg, Zn, Co$). It is found that primary alcohols and amines react preferentially at the hindered metal center. In the case of montmorillonite, maleic acid and methylmaleic acid were intercalated by a solid-state reaction, whereas their geometric isomers fumaric acid and methylfumaric acid were not. In ethanolic solution both acids were incorporated into the host.

Aluminum hydroxide, $Al(OH)_3$, exists in nature as three structural modifications: gibbsite, bayerite, and nordstrandite.[10−13] In gibbsite each of the $Al(OH)_3$ layers consists of nearly close packed OH^- ions in which the Al^{3+} ions occupy $^2/_3$ of the octahedral holes between alternate layers. Treatment with lithium chloride, LiCl, in water leads to intercalation of both the Li^+ and Cl^- ions into the host structure to give the layered double hydroxide $[LiAl_2(OH)_6]Cl\cdot H_2O$. We have recently solved and refined the structure of this intercalate and its dehydrated analogue, $[LiAl_2(OH)_6]Cl$, using combined synchrotron X-ray and neutron powder diffraction.[14] Both these intercalates consist of eclipsed $[LiAl_2(OH)_6]^+$ layers stacked along the *c*-axis with the chloride ions located at the cell edges midway between the $[LiAl_2(OH)_6]^+$ layers; the lithium ions are located in the vacant octahedral sites within the $Al(OH)_3$ layers. As such, these intercalation compounds represent rare examples of layered double hydroxides (LDH's) in which the metal cations are ordered within the hydroxide layers. In this paper we describe the ability of the LDH, $[LiAl_2(OH)_6]Cl\cdot H_2O$, to exhibit shape-selective intercalation reactions.

Experimental Section

Synthesis. $[LiAl_2(OH)_6]Cl\cdot H_2O$ was prepared by stirring a suspension of gibbsite in an aqueous solution containing a 3-fold molar excess of lithium chloride at 90 °C for 6 h. The ion exchange intercalates were synthesized by the reaction of $[[LiAl_2(OH)_6]Cl\cdot H_2O$ with a 3-fold excess of the disodium salts of fumaric (*trans*-but-2-enedioic acid), maleic (*cis*-but-2-enedioc acid), 1,2-, 1,3-, and 1,4-benzenedioic acids in aqueous solution at room temperature for 1 h. Complete reaction was indicated

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Table 1. Summary of the Elemental Microanalysis and Diffraction Data for the Intercalation Compounds

guest	stoichiometry	c lattice constant^a/Å	elemental microanalysis obsd	calcd
1,4-benzenedicarboxylate	$[LiAl_2(OH)_6]_2(C_8H_4O_4)\cdot xH_2O$ $x \approx 5.5$	14.2	C% 15.49 H% 4.51 Al% 16.94 Li% 2.18 Cl% 0.3	C% 16.31 H% 4.62 Al% 18.32 Li% 2.36 Cl% 0
1,3-benzenedicarboxylate	$[LiAl_2(OH)_6]_2(C_8H_4O_4)\cdot xH_2O$ $x \approx 4$	15.1	C% 15.54 H% 4.40	C% 16.83 H% 4.41
1,2-benzenedicarboxylate	$[LiAl_2(OH)_6]_2(C_8H_4O_4)\cdot xH_2O$ $x \approx 4$	15.0^b	C% 16.97 H% 4.80	C% 16.83 H% 4.41
fumarate	$[LiAl_2(OH)_6]_2(C_4H_2O_4)\cdot xH_2O$ $x \approx 4$	12.2	C% 9.90 H% 3.94	C% 10.01 H% 4.62
maleate	$[LiAl_2(OH)_6]_2(C_4H_2O_4)\cdot xH_2O$ $x \approx 4$	12.9	C% 9.26 H% 3.30	C% 10.01 H% 4.62

[a] Based on hexagonal cell, $\alpha = \beta = 90°$, $\gamma = 120°$, $a = b = 5.08$ Å. Values obtained from high-resolution XRD data measure on Siemens D5000 instrument. [b] Phase collapses on drying, giving a material with a c lattice constant of 11.8 Å.

by the absence of any Bragg peaks from the host lattice in the X-ray diffraction patterns and of Cl in the elemental microanalysis. The dicarboxylate ions were extracted from the host lattice by stirring with an excess of an aqueous solution of Na_2CO_3 at 60 °C overnight.

Measurements. Powder X-ray diffraction patterns were recorded on a Siemens D5000 diffractometer equipped with a linear position-sensitive detector using Cu Kα_1 radiation in transmission geometry. In situ energy-dispersive X-ray diffraction data of the competition reactions were collected on Station 16.4 of the U.K. Synchrotron Radiation Source at Daresbury Laboratory using an experimental setup reported previously.[15,16] The guest solutions (approximately 0.1 M) were injected into an ampoule containing a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ at a rate of 0.2 mL/min from a SAGE Instruments syringe pump. Individual spectra were collected with acquisition times of 60 s and a fixed detector angle ($2\theta = 1.58°$). Analysis of the growth of the diffraction peaks was performed by integrating the peak intensitites using a Gaussian fitting routine.[17] ^1H NMR spectra were recorded on a Brüker AM-300 spectrometer [^1H (300 MHz)]. Spectra were referenced internally using the residual solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm).

Results and Discussion

$[LiAl_2(OH)_6]Cl\cdot H_2O$ has been shown to undergo a wide range of facile anion-exchange reactions with a variety of inorganic and organic guests.[18−21] For example, treatment of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with an aqueous solution of the disodium salt of fumaric acid yields the first-stage intercalate $[LiAl_2(OH)_6]_2[trans\text{-}C_4H_2O_4]\cdot 4H_2O$. The measured interlayer separation of 12.1 Å and the host:guest ratio are consistent with ordering of the guest ions at approximately 90° to the $[LiAl_2(OH)_6]^+$ layers. Similarly, treatment of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with the disodium salt of maleic acid yields the first stage intercalate $[LiAl_2(OH)_6]_2[cis\text{-}C_4H_2O_4]\cdot 4H_2O$. The elemental microanalytical and diffraction data for all the intercalation compounds are summarized in Table 1.

However, when an equimolar aqueous solution of the disodium salts of fumaric and maleic acids are stirred with a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ for 1 h, the X-ray powder diffraction pattern is identical with a sample prepared by direct intercalation with pure disodium fumarate, there is no evidence for any Bragg reflections assignable to other intercalated phases. This observation suggests that disodium fumarate is selectively intercalated into $[LiAl_2(OH)_6]Cl\cdot H_2O$. To confirm and quantify this shape-selective intercalation behavior, we have studied this reaction using both solution NMR and in situ X-ray powder diffraction.

We can conveniently follow the uptake of the dicarboxylate ions during the course of the intercalation reaction using solution ^1H NMR spectroscopy. For example, if an equimolar solution of the dicarboxylate isomers was added to a suspension of $[LiAl_2(OH)_6]Cl\cdot D_2O$ in D_2O, after 20 min only the C*H* resonance due to the fumarate ions is observed to decrease significantly in intensity, indicating that fumarate is being selectively incorporated into the layered double hydroxide (Figure 1). Intercalation of these ions between the $[LiAl_2(OH)_6]^+$ layers means that these molecules now have such long correlation times that their ^1H NMR resonances are sufficiently broadened that they are not observed in a conventional solution NMR experiment. Integration of the ^1H NMR signal due to the C*H* resonance of the maleate ions against an internal standard of acetonitrile allows the selectivity for fumarate intercalation was estimated to be in excess of 98%.

The fumarate ions can be ion-exchanged out of $[LiAl_2(OH)_6]_2[trans\text{-}C_4H_2O_4]\cdot 4H_2O$ by addition of an excess of an aqueous solution of Na_2CO_3 to the solid (Figure 2a) yielding the carbonate intercalate $[LiAl_2(OH)_6]_2CO_3\cdot xH_2O$. The solution ^1H NMR of the reaction washings showed only the C*H* resonance due to the fumarate anions confirming the selectivity of the reaction.[22]

Reaction of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with either disodium salts of 1,2-, 1,3-, or 1,4-benzenedioic acids in H_2O yields the intercalation compounds $[LiAl_2(OH)_6]_2[G]\cdot x\ H_2O$ ($x = 4$ or 5; G = 1,2-$C_8H_4O_4$, 1,3-$C_8H_4O_4$, 1,4-$C_8H_4O_4$), respectively. A summary of the elemental microanalytical and diffraction data for all these compounds is given in Table 1. However, when an equimolar solution

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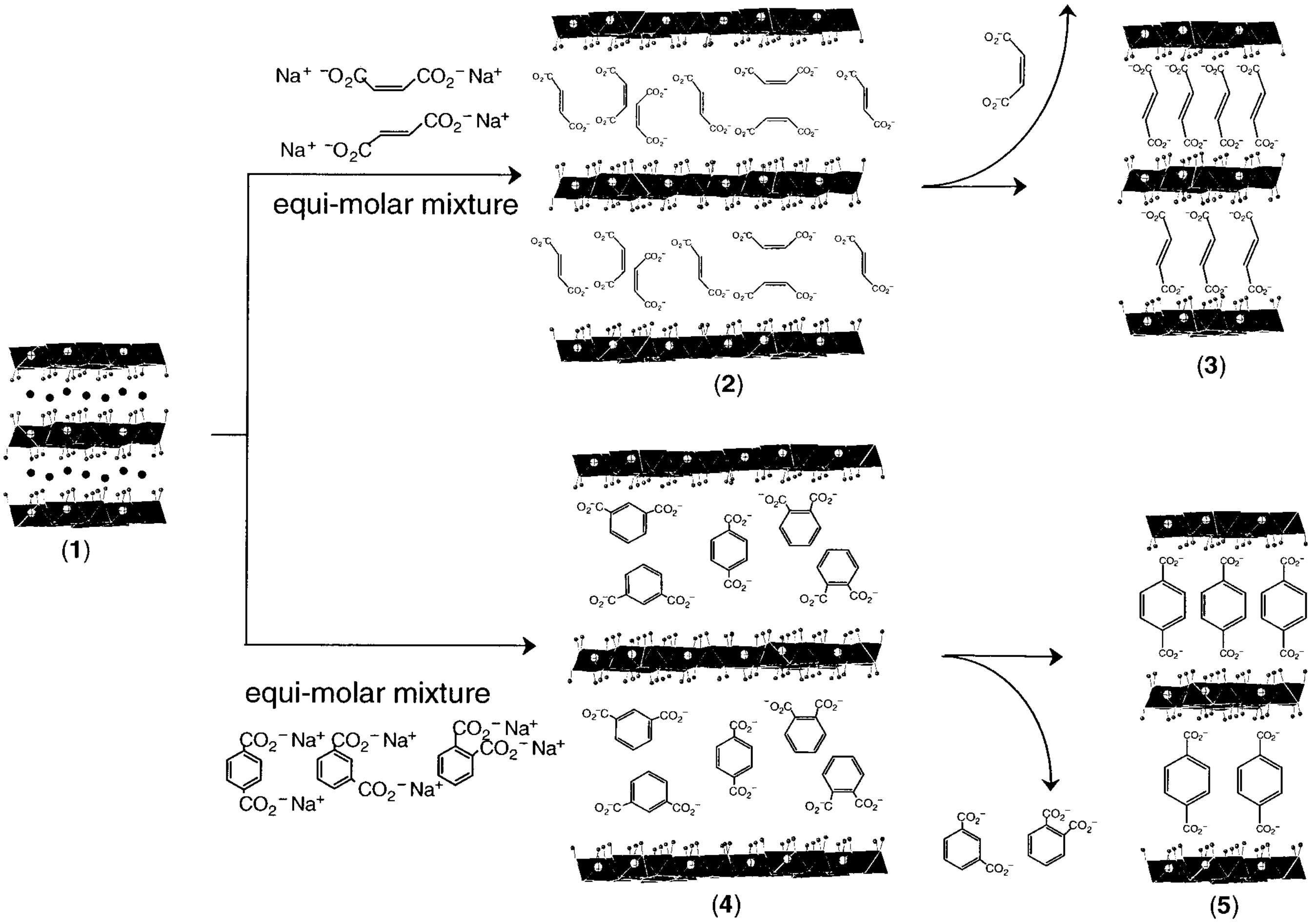

Figure 1. Schematic diagram showing the kinetic and thermodynamic intercalate phases, $[LiAl_2(OH)_6]_2(C_8H_4O_4)\cdot xH_2O$ (**4**), $[LiAl_2(OH)_6]_2(1,4\text{-}C_8H_4O_4)\cdot xH_2O$ (**5**), $[LiAl_2(OH)_6]_2(C_4H_2O_4)\cdot xH_2O$ (**2**), $[LiAl_2(OH)_6]_2(\textit{trans}\text{-}C_4H_2O_4)\cdot xH_2O$ (**3**) formed on intercalation of dicarboxylate anions into $[LiAl_2(OH)_6]Cl\cdot H_2O$ (**1**). The illustration of the packing of the various isomers between the $[LiAl_2(OH)_6]^+$ layer is schematic.

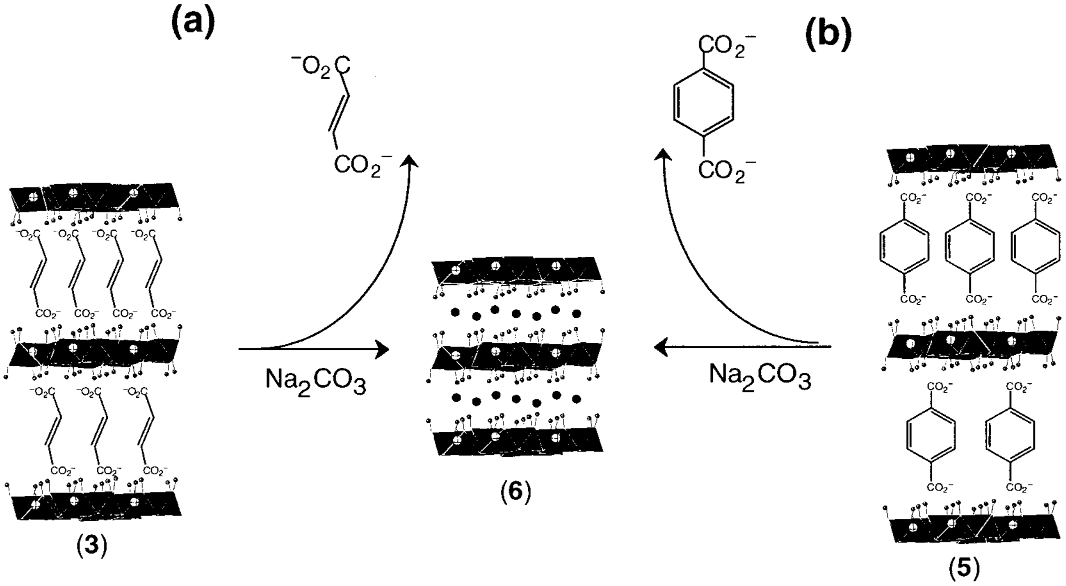

Figure 2. (a) Ion-exchange of $[LiAl_2(OH)_6]_2[\textit{trans}\text{-}C_4H_2O_4]\cdot 4H_2O$ (**3**) with Na_2CO_3 giving $[LiAl_2(OH)_6]_2CO_3\cdot H_2O$ (**6**). (b) Ion-exchange of $[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4]\cdot 5H_2O$ (**5**) with Na_2CO_3 giving $[LiAl_2(OH)_6]_2CO_3\cdot H_2O$ (**6**).

of all three disodium salts is added to $[LiAl_2(OH)_6]Cl\cdot H_2O$ only $[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4]\cdot 4H_2O$ is isolated from the reaction. The XRD of this material is identical with a sample prepared by direct reaction of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with $1,4\text{-}C_8H_4O_4$. We have again been able to follow this reaction by solution ^1H NMR. On addition of an equimolar solution of all three dicarboxylic ions to a suspension of $[LiAl_2(OH)_6]Cl\cdot D_2O$ in D_2O only the ^1H resonances assignable to the $1,4\text{-}C_8H_4O_4$ isomer decreased significantly in intensity during the

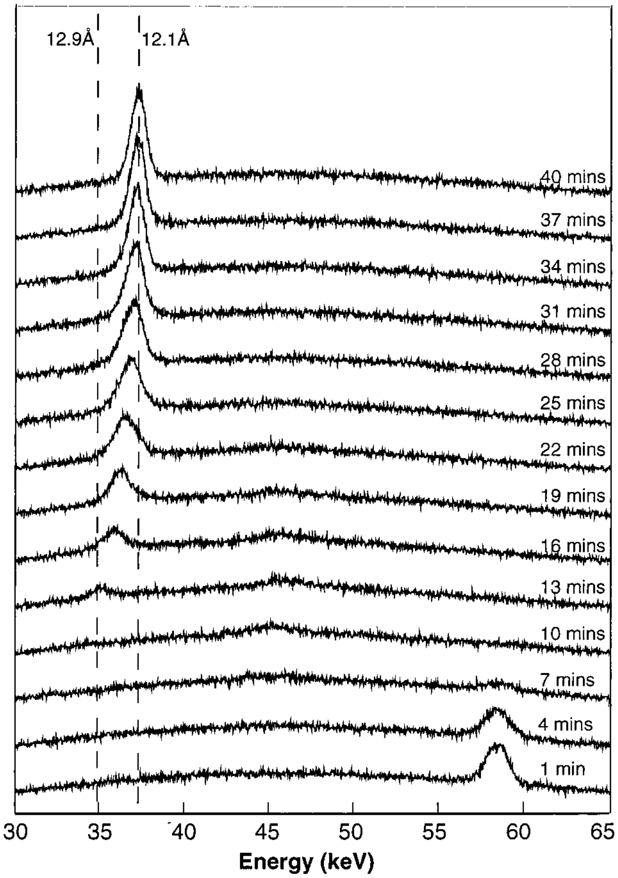

Figure 3. Time-resolved, in situ, energy-dispersive X-ray powder diffraction patterns of $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ during injection of an equimolar mixture of the disodium salts of fumaric and maleic acids.

course of the reaction, indicating their incorporation into the LDH. We were also able to ion-exchange the intercalated ions out of this materials by stirring with Na_2CO_3 in water overnight (Figure 2b). The solution ^1H NMR of the supernatant solution following ion-exchange was dominated by resonances due to the 1,4-$C_8H_4O_4$, though a small amount of the 1,2-$C_8H_4O_4$ was also observed.[22] The degree of selectivity for 1,4-$C_8H_4O_4$ intercalation into $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ was estimated to be in excess of 95%.

We have also investigated the selective intercalation of these dicarboxylates using time-resolved in situ energy-dispersive X-ray diffraction (EDXRD). These experiments confirmed that these reactions are remarkably facile with a typical half-life ($t_{1/2}$) ca. 1−2 min at room temperature. To slow these reactions down sufficiently to allow us to study their evolution detail, it was necessary to add the guest solution to an aqueous suspension of the host lattice in a dropwise manner via a syringe pump. Figure 3 shows a series of EDXRDs as an equimolar mixture of disodium fumarate and maleate was added to $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ (7.65 Å, 57.0 keV) at a rate of 0.2 mL min^{-1}. While this experimental setup prevents us from performing a quantitative kinetic analysis of the data, it did reveal a number of important insights into these regioselective reactions.

At the early stage of the reaction we were able to observe a crystalline intermediate phase which exhibits a broad Bragg reflection centered at 10.0 Å (44.9 keV). This phase has subsequently been isolated in the laboratory, and the observed reflection corresponds to the (002) of the second-stage intercalate $[LiAl_2(OH)_6]_4[Cl]_2[C_4H_2O_4]{\cdot}xH_2O$. Further details of this and other second-stage intermediates will be given elsewhere.[23]

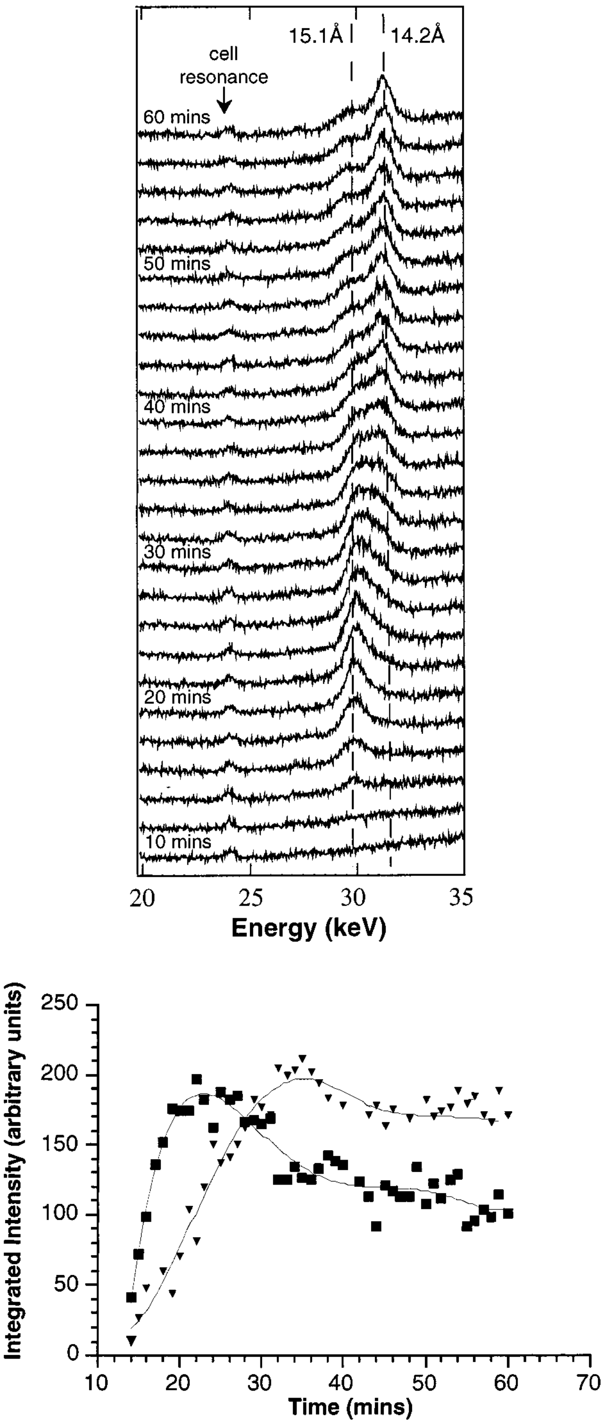

Figure 4. (a, top) Time-resolved, in situ, energy-dispersive X-ray powder diffraction patterns of $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ during injection of an equimolar mixture of the disodium salts of 1,2-, 1,3-, and 1,4-benzenedicarboxylate acids in H_2O at room temperature. (b, bottom) Integrated intensity of the Bragg peaks at 15.1 Å (29.8 keV) and 14.3 Å (31.3 keV) as a function of time during the addition of all three benzenedicarboxylate ions. The solid lines are a guide to the eye and have no physical significance.

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On continued addition of the dicarboxylate ions another crystalline phase appears in the EDXRD. This material has an interlayer spacing of 12.9 Å (34.9 keV) corresponding to the (001) of the maleate intercalate, which then undergoes rapid exchange with fumarate anions. This manifests itself as a shift in the peak position to 12.2 Å (37.1 keV), the 001 of the fumarate intercalate. If the guests are intercalated separately, the same product Bragg reflections grow in smoothly at constant energy values, indicating that the shift of the peak positions in the competition reaction is due to exchange and not as a result of guest reorientation as has been observed in other systems.[24] The *d* spacings observed in these runs are given in Table 1. It is likely, however, that the initial phase is not the pure maleate intercalate but contains a mixture of the anions in the interlayer region, and one therefore observes the larger *d* spacing. This kinetic phase then rapidly collapses with expulsion of the maleate anions and the subsequent formation of a close-packed, phase-pure fumarate intercalate, identical with that observed as the final product in the laboratory experiments. Since the lithium ions are ordered within the gibbsite layers the observed selectivity may stem from differing packing energies of the guests within the interlayer region and their interactions with the positively charged $[LiAl_2(OH)_6]^+$ layers. This reaction is shown schematically in Figure 1.

We have also investigated the selective intercalation of the benzenedicarboxylate isomers into $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ using time-resolved, in situ EDXRD. Again second-stage intermediates are observed at the very early stages of the addition of the anions. In this case the kinetic phase has a *d* spacing of 15.1 Å (29.8 keV) corresponding to the interlayer spacing of either the 1,2-benzenedicarboxylate or the 1,3-benzenedicarboxylate intercalate, which then collapses to the 1,4-benzenedicarboxylate intercalate giving a final product phase at 14.2 Å (31.3 keV) in agreement with the laboratory observations. The growth of the product peaks is shown in the stack plot in Figure 4. The experimental setup prevented a large enough excess of the guests to drive the reaction to completion being used resulting in a small amount of the initial phase remaining at the end of the reaction. As before it is likely that in the initial phase all three isomers are intercalated with subsequent deintercalation of the 1,2- and 1,3-benzenedicarboxylates yielding the observed product.

Conclusion

$[LiAl_2(OH)_6]Cl{\cdot}H_2O$ has been shown to undergo highly regioselective intercalation reactions with equimolar mixtures of isomeric dicarboxylate anions. In situ energy-dispersive X-ray diffraction studies suggest that the reactions involve the initial kinetic insertion of all the isomers followed by collapse to the most stable intercalate phase as a result of expelling the disfavored anions. In both the systems studied, the favored isomer seems to be the one which can interact most favorably with the adjacent $[LiAl_2(OH)_6]^+$ layers.

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Supporting Information Available: Indexing tables of the intercalates (3 pages). Ordering information is given on any current masthead page.

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