# Formation of Second-Stage Intermediates in Anion-Exchange Intercalation Reactions of the Layered Double Hydroxide $[LiAl_2(OH)_6]Cl\cdot H_2O$ As Observed by Time-Resolved, in Situ X-ray Diffraction

Andrew M. Fogg, Jenifer S. Dunn, and Dermot O'Hare*,†

*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road,*
*Oxford OX1 3QR, U.K.*

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Time-resolved in situ energy-dispersive X-ray diffraction studies on the intercalation of dicarboxylate anions ($Na_2C_4H_4O_4$, $Na_2C_6H_8O_4$, $Na_2$-*trans*-$C_4H_2O_4$, $Na_2$-*cis*-$C_4H_2O_4$, $Na_2$-L-$C_4H_4O_5$, $Na_2$-1,2-$C_8H_4O_4$, $Na_2$-1,4-$C_8H_4O_4$) into $[LiAl_2(OH)_6]Cl\cdot H_2O$ have revealed the rapid formation of a second-stage intermediate phase that subsequently transforms into a phase-pure fully ion-exchanged product. These intermediates can be isolated as pure crystalline phases by reaction of the host lattice with stoichoimetric amounts of the dicarboxylate anions.

## Introduction

The isolation of ordered intercalation compounds in which the layers are partially filled with guest ions or molecules is known as staging and is one of the most fascinating aspects of the intercalation chemistry of lamellar materials. In particular, the literature describing graphite intercalation reactions contains numerous examples of staging intermediates.[1,2] However, staging in host lattices other than graphite is much less common but has been observed on a few occasions for transition metal dichalcogenides.[1,3−5] The classical description of staging, proposed by Rüdorff, involves the filling of every *n*th layer in the *n*th stage compound (Figure 1).[6] This model, however, cannot explain transformations from odd to even stages without a deintercalation−intercalation mechanism. In reality, it is believed that these reactions occur via a domain model first proposed by Daumas and Hérold and are shown schematically in Figure 1.[7] This model consists of islands of intercalate located in distorted regions of the host diffusing toward the crystallite center. The common occurrence of this phenomenon in graphite is thought to be as a consequence of the flexible nature of the graphite sheets.

Theoretical models of staging typically divide the host lattices into three classes based on the thickness of the layers ranging from single atom layers (e.g., graphite, boron nitride) to rigid, many atom thick layers as found in clays with transition metal dichalcogenides belonging to the intermediate class.[8] Calculations on these models indicate that staging can occur readily in graphite intercalation compounds but should not be observed in clays.[9]

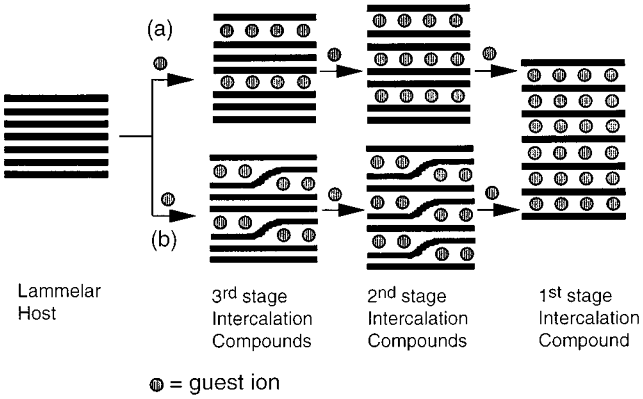

**Figure 1.** Schematic diagram showing the formation of the staged intercalation compounds for lamellar hosts: (a) model proposed by Rüdorff; (b) model proposed by Daumas and Hérold.

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 the 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

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**Table 1. Summary of the Elemental Microanalysis and Diffraction Data for the First-Stage Intercalation Compounds**

| | | | elemental microanalysis | |
|---|---|---|---|---|
| guest | stoichiometry of first-stage intermediate | *c*-lattice constant[a] (Å) | obsd (%) | calcd (%) |
| succinate | $[LiAl_2(OH)_6]_2[C_4H_4O_4]\cdot xH_2O$<br>$x \approx 8$ | 12.1 | C, 8.44 | C, 8.20 |
| | | | H, 5.25 | H, 5.50 |
| | | | Li, 2.39 | Li, 2.37 |
| | | | Al, 17.77 | Al, 18.41 |
| adipate | $[LiAl_2(OH)_6]_2[C_6H_8O_4]\cdot xH_2O$<br>$x \approx 8$ | 14.2 | C, 12.06 | C, 12.47 |
| | | | H, 5.48 | H, 5.58 |
| | | | Li, 2.32 | Li, 2.26 |
| | | | Al, 16.24 | Al, 17.57 |
| fumarate | $[LiAl_2(OH)_6]_2[\textit{trans}\text{-}C_4H_2O_4]\cdot xH_2O$<br>$x \approx 4$ | 12.2 | C, 9.90 | C, 10.01 |
| | | | H, 3.94 | H, 4.62 |
| maleate | $[LiAl_2(OH)_6]_2[\textit{cis}\text{-}C_4H_2O_4]\cdot xH_2O$<br>$x \approx 4$ | 12.9 | C, 9.26 | C, 10.01 |
| | | | H, 3.30 | H, 4.62 |
| L-malate | $[LiAl_2(OH)_6]_2[\text{L-}C_4H_4O_5]\cdot xH_2O$<br>$x \approx 7$ | 12.1 | C, 8.50 | C, 8.77 |
| | | | H, 4.01 | H, 4.78 |
| | | | Al, 20.11 | Al, 19.69 |
| | | | Li, 2.53 | Li, 2.53 |
| phthalate | $[LiAl_2(OH)_6]_2[1,2\text{-}C_8H_4O_4]\cdot xH_2O$<br>$x \approx 4$ | 15.0[b] | C, 16.97 | C, 16.83 |
| | | | H, 4.80 | H, 4.41 |
| terephthalate | $[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4]\cdot xH_2O$<br>$x \approx 5.5$ | 14.2 | C, 15.49 | C, 16.31 |
| | | | H, 4.51 | H, 4.62 |
| | | | Al, 16.94 | Al, 18.32 |
| | | | Li, 2.18 | Li, 2.36 |

[a] Based on hexagonal cell, $\alpha = \beta = 90°$, $\gamma = 120°$, $a = b \approx 5.08$ Å. Values obtained from high-resolution XRD data were measured on a Siemens D5000 diffractometer. [b] Collapses to 11.8 Å on drying.

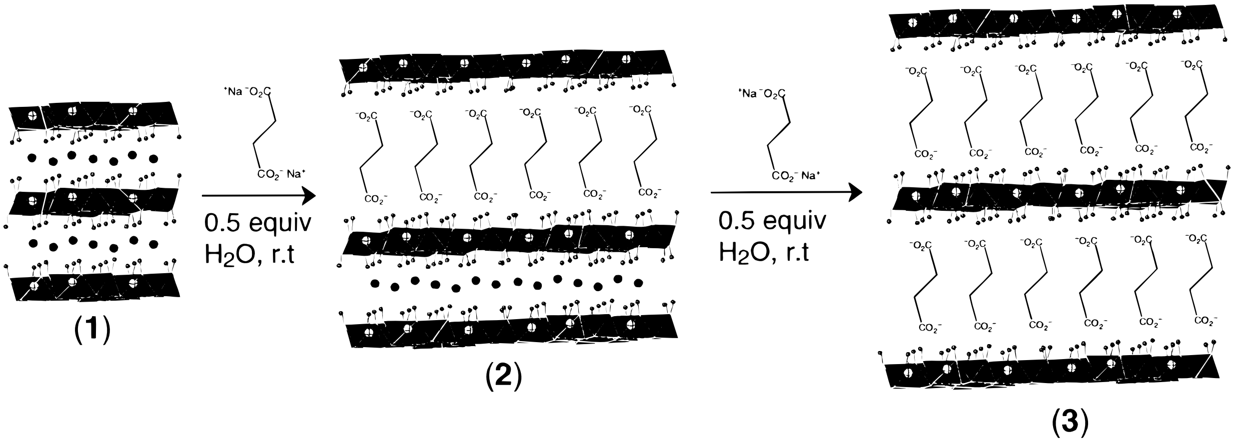

**Figure 2.** Schematic diagram showing the intercalation of the succinate anions into $[LiAl_2(OH)_6]Cl\cdot H_2O$ (**1**), giving $[LiAl_2(OH)_6]_4[C_4H_4O_4][Cl]_2\cdot xH_2O$ (**2**) and subsequently $[LiAl_2(OH)_6]_2[C_4H_4O_4]\cdot xH_2O$ (**3**). The observed interlayer separation is required for the ions to adopt the orientation shown.

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 form second-stage intermediates during the ion-exchange reactions with dicarboxylate salts.

## Experimental Section

$[LiAl_2(OH)_6]Cl\cdot H_2O$ 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 first-stage ion-exchange intercalates were synthesized by the reaction of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with a 3-fold molar excess of the disodium salt of the required dicarboxylic acid ($Na_2C_4H_4O_4$, $Na_2C_6H_8O_4$, $Na_2\text{-}\textit{trans}\text{-}C_4H_2O_4$, $Na_2\text{-}\textit{cis}\text{-}C_4H_2O_4$, $Na_2\text{-L-}C_4H_4O_5$, $Na_2\text{-}1,2\text{-}C_8H_4O_4$, $Na_2\text{-}1,4\text{-}C_8H_4O_4$) (see Table 1) in aqueous solution at room temperature for 1 h. Complete reaction was indicated by the absence of any Bragg peaks from the host lattice in the powder X-ray diffraction patterns and the absence of $Cl^-$ in the elemental microanalysis. The second-stage intermediates were prepared by stirring a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with the required stoichiometric amount of the guest for the second-stage intermediate at room temperature for 15 min.

**Measurements.** Powder X-ray diffraction patterns were recorded on a Siemens D5000 powder diffractometer using Cu K$\alpha$ radiation. In situ energy-dispersive X-ray diffraction data for the 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] Aqueous solu-

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**Table 2. Summary of the Elemental Microanalysis and Diffraction Data for the Second-Stage Intercalation Compounds**

| guest | stoichiometry of second-stage intermediate | *c*-lattice constant[a] (Å) | elemental microanalysis | |
|---|---|---|---|---|
| | | | obsd (%) | calcd (%) |
| succinate | $[LiAl_2(OH)_6]_4[Cl]_2[C_4H_4O_4]\cdot xH_2O$<br>$x \approx 7$ | 19.6 | C, 5.05<br>H, 6.11<br>Li, 2.90<br>Al, 22.90<br>Cl, 6.48 | C, 4.98<br>H, 4.39<br>Li, 2.88<br>Al, 22.37<br>Cl, 7.35 |
| adipate | $[LiAl_2(OH)_6]_4[Cl]_2[C_6H_8O_4]\cdot xH_2O$<br>$x \approx 6$ | 22.0 | C, 7.78<br>H, 4.68<br>Li, 2.54<br>Al, 21.65<br>Cl, 5.65 | C, 7.39<br>H, 4.55<br>Li, 2.85<br>Al, 22.14<br>Cl, 7.27 |
| fumarate | $[LiAl_2(OH)_6]_4[Cl]_2[\textit{trans}\text{-}C_4H_2O_4]\cdot xH_2O$<br>$x \approx 8$ | 19.7 | C, 4.80<br>H, 4.18<br>Cl, 7.07 | C, 4.90<br>H, 4.32<br>Cl, 7.23 |
| maleate | $[LiAl_2(OH)_6]_4[Cl]_2[\textit{cis}\text{-}C_4H_2O_4]\cdot xH_2O$<br>$x \approx 8$ | 21.1 | C, 4.21<br>H, 4.32<br>Cl, 8.85 | C, 4.90<br>H, 4.32<br>Cl, 7.23 |
| L-malate | $[LiAl_2(OH)_6]_4[Cl]_2[\text{L-}C_4H_4O_5]\cdot xH_2O$<br>$x \approx 13$ | 19.9 | C, 4.24<br>H, 4.79<br>Al, 20.95<br>Li, 2.43<br>Cl, 6.08 | C, 4.41<br>H, 5.00<br>Al, 19.82<br>Li, 2.55<br>Cl, 6.51 |
| phthalate | $[LiAl_2(OH)_6]_4[Cl]_2[1,2\text{-}C_8H_4O_4]\cdot xH_2O$<br>$x \approx 7$ | 22.6 | C, 10.36<br>H, 4.35<br>Cl, 6.37 | C, 9.49<br>H, 4.18<br>Cl, 7.00 |
| terephthalate | $[LiAl_2(OH)_6]_4[Cl]_2[1,4\text{-}C_8H_4O_4]\cdot xH_2O$<br>$x \approx 10$ | 21.9 | C, 8.51<br>H, 4.44<br>Cl, 7.53 | C, 9.01<br>H, 4.53<br>Cl, 6.65 |

[a] Based on hexagonal cell, $\alpha = \beta = 90°$, $\gamma = 120°$, $a = b \approx 5.08$ Å. Values obtained from high-resolution XRD data were measured on a Siemens D5000 diffractometer. Measured d spacings from the in situ EDXRD data vary by up to 0.1 Å.

tions of the guests (approximately 0.1 M) were injected into an ampoule containing a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ in water 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 ($2\theta = 1.58°$).

## 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.[17-20] For example, treatment of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with the disodium salt of succinic acid ($Na_2C_4H_4O_4$) yields the first-stage intercalate $[LiAl_2(OH)_6]_2[C_4H_4O_4]\cdot xH_2O$ ($x = 4-5$). The observed interlayer separation of 12.1 Å is is required if the guests are to adopt an orientation of approximately 90° to the $[LiAl_2(OH)_6]^+$ layers (Figure 2). The XRD data is not of sufficently high quality to allow us to carry out either a full or partial structure determination. Therefore, we are unable to determine if all the guests adopt this orientation. Similar orientations can be inferred for other guests from their observed *d* spacing.

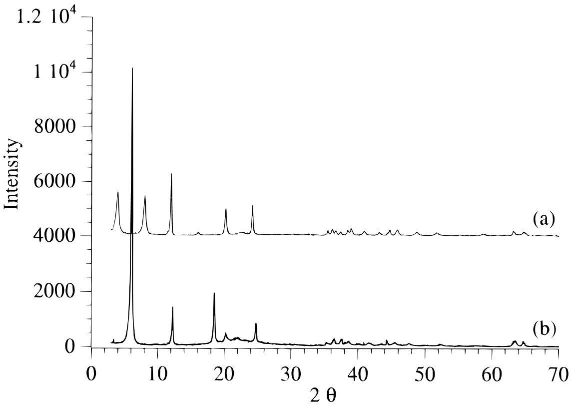

**Figure 3.** X-ray diffraction patterns of (a) $[LiAl_2(OH)_6]_4[C_6H_8O_4][Cl]_2\cdot xH_2O$ and (b) $[LiAl_2(OH)_6]_2[C_6H_8O_4]\cdot xH_2O$.

We have investigated the intercalation of a range of dicarboxylate salts ($Na_2C_4H_4O_4$, $Na_2C_6H_8O_4$, $Na_2$-*trans*-$C_4H_2O_4$, $Na_2$-*cis*-$C_4H_2O_4$, $Na_2$-L-$C_4H_4O_5$, $Na_2$-1,2-$C_8H_4O_4$, $Na_2$-1,4-$C_8H_4O_4$) into $[LiAl_2(OH)_6]Cl\cdot H_2O$ using time-resolved in situ energy-dispersive X-ray diffraction (EDXRD). These studies revealed that these exchange reactions occur very readily, typically with a half-life of 1−2 min, at room temperature, so in order to study these reactions in more detail it was necessary to add a solution containing the guest ions in a dropwise manner via a syringe pump. While this experimental setup prevents a full quantitative kinetic analysis of the reactions it did reveal evidence for previously unobserved staging intermediates. Figure 4 shows the EDXRD data as a function of time during the addition of $Na_2C_4H_4O_4$ to a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ in water. The immediate decay of the 001 Bragg reflection due to $[LiAl_2(OH)_6]Cl\cdot H_2O$ (57.0 keV $\equiv d_{\text{spacing}} = 7.65$ Å) following the addition of the guest solution is accompanied by the growth of a Bragg reflection at 44.7 keV ($d_{\text{spacing}} = 9.9$ Å). This reflection can be assigned to the 002 reflection of the second-stage intermediate $[LiAl_2(OH)_6]_4[C_4H_4O_4]Cl_2\cdot xH_2O$ ($x \approx 7$). Growth of the 001 reflection of the first-stage product $[LiAl_2(OH)_6]$-

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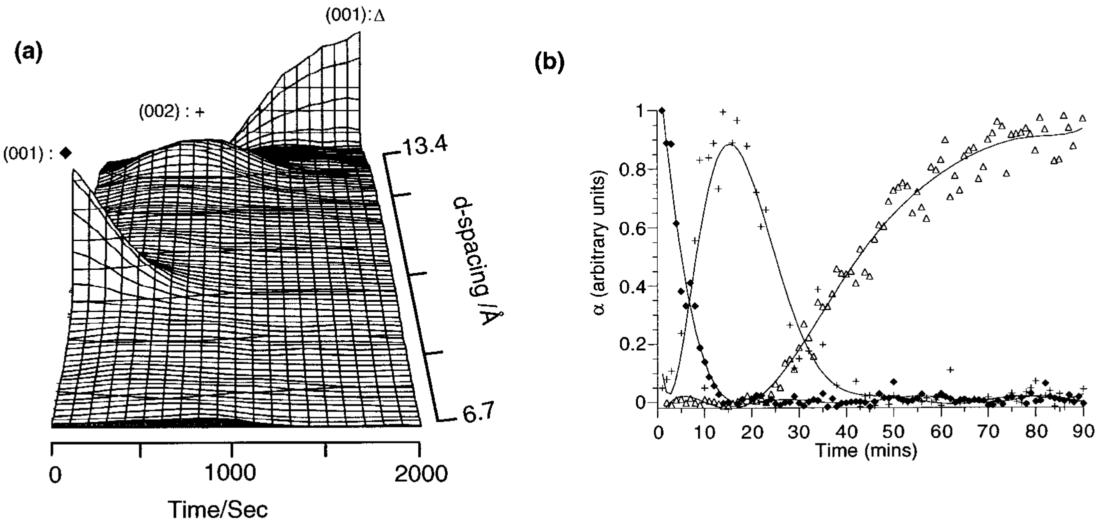

**Figure 4.** Time-resolved, in situ, energy-dispersive X-ray powder diffraction data showing the course of the ion-exchange reaction between $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ and disodium succinate: (a) 3D stacked plot; (b) plot of integrated intensity of 001 reflection of the host (◆), 002 reflection of the second-stage intermediate (+) and 001 reflection of the final phase (△) as a function of time.

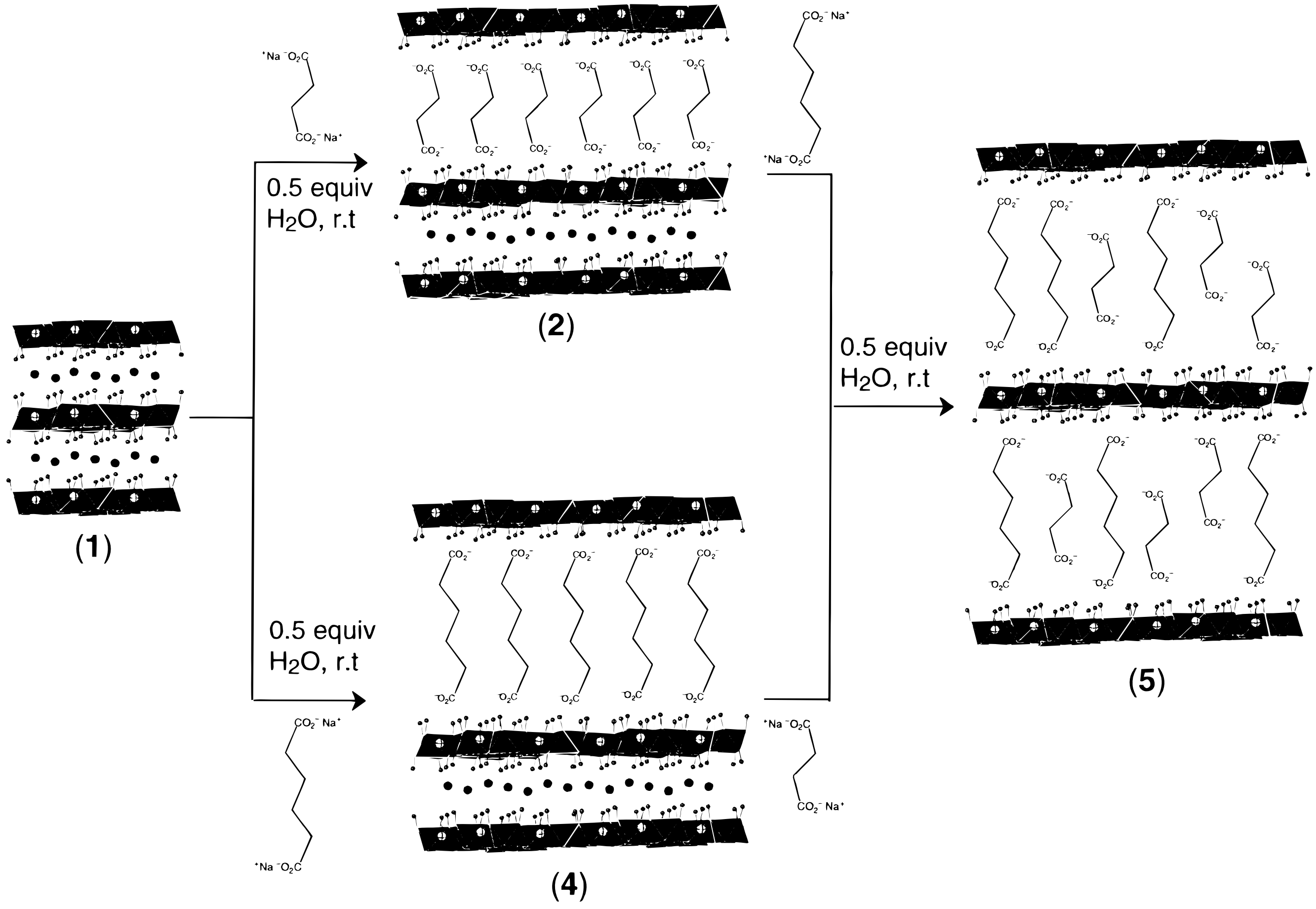

**Figure 5.** Schematic diagram of the crossover intercalation reactions between $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ (**1**) and the disodium salts of succinic and adipic acids giving $[LiAl_2(OH)_6]_4[C_4H_4O_4][Cl]_2{\cdot}xH_2O$ (**2**) and $[LiAl_2(OH)_6]_4[C_6H_8O_4][Cl]_2{\cdot}xH_2O$ (**4**), respectively. Both **2** and **4** ultimately yield $[LiAl_2(OH)_6]_2[C_4H_4O_4]_{0.5}[C_6H_8O_4]_{0.5}{\cdot}xH_2O$ (**5**).

$[C_4H_4O_4]{\cdot}xH_2O$, (36.3 keV $\equiv d_{\text{spacing}} = 12.1$ Å) is not observed until the intermediate has gone through its maximum and the host has decayed completely. No other reflections were observed that could be assigned to higher order staging intermediates. Similarly, this behavior has been observed for the intercalation of $Na_2C_6H_8O_4$, $Na_2$-*trans*-$C_4H_2O_4$, $Na_2$-*cis*-$C_4H_2O_4$, $Na_2$-L-$C_4H_4O_5$, $Na_2$-1,2-$C_8H_4O_4$, and $Na_2$-1,4-$C_8H_4O_4$, respectively, into $[LiAl_2(OH)_6]Cl{\cdot}H_2O$, and the full analytical and XRD data for the first- and second-stage intercalates are summarized in Tables 1 and 2.

The second-stage intermediates can be isolated by reaction with a stoichiometric amount of the required guest and are crystalline phases with the *d* spacings expected from the sum of the *d* spacings of the two guests. In most cases, trace amounts of either the host lattice or the first-stage product were present in the diffraction pattern. The XRD patterns for both $[LiAl_2(OH)_6]_4[C_6H_8O_4]Cl_2 \cdot 6H_2O$ and $[LiAl_2(OH)_6]_2[C_6H_8O_4] \cdot 6H_2O$ are given in Figure 3.

Crossover reactions in which a second-stage intermediate of guest A is reacted with a stoichiometric amount of guest B and vice versa have been performed. If these intermediate phases are indeed ordered second-stage intercalates then the final isolated material from these crossover reactions should be independent of the order in which the guests are intercalated as shown schematically in Figure 5. What we in fact observe is the same single intercalated phase in which the interlayer spacing is that expected for the largest anion used. When these reactions are carried out with an excess of guest B complete exchange occurs with the product being that of guest B. The potential of exchange for both intercalated guests is likely to lead to each layer containing a mixture of the dicarboxylate guests in the crossover products rather than the expanded structure where the individual guests occupy alternate layers.

We have attempted to isolate higher order staged intermediates in these reactions by reaction the host lattice with 0.33 and smaller molar equivalents of guest anions. In all cases the diffraction data showed only the presence of the corresponding second-stage intermediate and the host lattice, $[LiAl_2(OH)_6]Cl \cdot H_2O$.

## Conclusion

We have demonstrated that the LDH, $[LiAl_2(OH)_6]Cl \cdot H_2O$, exhibits staging during the intercalation reactions with dicarboxylate anions. This represents an extremely rare example of this phenonena in hydrotalcite-type minerals. The time-resolved in situ studies also indicate the stepwise fromation of these phases and then conversion into fully ion-exchanged phases. Given the inherent rigid nature of the $[LiAl_2(OH)_6]^+$ layers it is likely that the staging in this system can be explained by the Rüdorff model where every second layer contains the dicarboxylate guest rather than by the Daumas–Hérold model, which would require buckling of the layers.

**Acknowledgment.** We would like to thank EPSRC for financial support and access to the Synchrotron Radiation Source at Daresbury Laboratory, U.K.

**Supporting Information Available:** XRD data ($I_{obs}$, $2\theta$, assignment) for all the intercalation compounds given in Tables 1 and 2 (15 pages). Ordering information is given on any current masthead page.

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