

# Synthesis and Anion Exchange Chemistry of Rhombohedral Li/Al Layered Double Hydroxides

Andrew M. Fogg,\* Amal J. Freij, and Gordon M. Parkinson

A. J. Parker Cooperative Research Centre for Hydrometallurgy, School of Applied Chemistry, Curtin University of Technology, P.O. Box U1987, Perth 6845, Australia

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A new Li/Al layered double hydroxide,  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ , having a rhombohedral layer stacking sequence has been synthesized by the reaction of the  $\text{Al}(\text{OH})_3$  polymorphs, bayerite and nordstrandite, with LiCl. As is the case with the hexagonal analogue, rhombohedral  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$  has been found to readily undergo anion exchange reactions with a range of dicarboxylate anions although these reactions differ significantly in that no crystalline staging intermediates could be isolated. The rhombohedral stacking is maintained in the dicarboxylate derivatives.

Layered double hydroxides (LDHs) are unusual among intercalation hosts, in that they contain positively charged layers with exchangeable interlayer anions and, as a result, have been the subject of numerous studies. The formula of these compounds can be generalized to  $[\text{M}^{z+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^\xi \text{X}^{n-}_{\xi/n} \cdot n\text{H}_2\text{O}$ . In the vast majority of cases,  $z = 2$  in which case  $\text{M}^{2+} = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}$ , or  $\text{Cu}^{2+}$  and  $\text{M}^{3+} = \text{Al}^{3+}, \text{Cr}^{3+}, \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Ga}^{3+}, \text{Co}^{3+}, \text{Ni}^{3+}, \text{V}^{3+}$ , or  $\text{Sc}^{3+}$  giving  $\xi = x^{1-3}$ . LDHs have also been prepared with  $z = 1$ . In this case,  $\text{M}^+$  is limited to  $\text{Li}^+$  and  $\text{M}^{3+} = \text{Al}^{3+}$ .<sup>4–7</sup> Structurally, LDHs are related to brucite ( $\text{Mg}(\text{OH})_2$ ),<sup>8</sup> with the replacement of some of the  $\text{Mg}^{2+}$  cations by trivalent ions creating the positively charged layers which can be stacked either rhombohedrally or hexagonally. Both of these stacking sequences have been observed in nature, with hydrotalcite ( $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$ ) and pyroaurite ( $\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3\cdot 4.5\text{H}_2\text{O}$ ) being rhombohedral while manasseite and sjörgenite are their hexagonal analogues, respectively.<sup>9–11</sup>

The structures of the Li/Al LDHs  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot \text{H}_2\text{O}$  and  $[\text{LiAl}_2(\text{OH})_6]\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$ ), formed by the intercalation of gibbsite ( $\gamma\text{-Al}(\text{OH})_3$ ), have been determined by Rietveld refinement as being hexagonal.<sup>4</sup> In these compounds, the  $\text{Li}^+$  cations occupy the vacant octahedral sites within the  $\text{Al}(\text{OH})_3$  layers and the

$[\text{LiAl}_2(\text{OH})_6]^+$  layers are eclipsed along the  $c$ -axis. This is in agreement with observations made on Li/Al LDHs synthesized via the precipitation route.<sup>6,7</sup> In the structure of  $[\text{LiAl}_2(\text{OH})_6]\text{OH}\cdot 2\text{H}_2\text{O}$ , it was found that there was ordering of the cations within each  $[\text{LiAl}_2(\text{OH})_6]^+$  layer but random stacking of the layers giving rise to a 54-layer structural model.<sup>12</sup>

Li/Al LDHs have been shown to undergo anion exchange reactions with a wide variety of inorganic and organic species, with the chloride and nitrate intercalates being found to be the most versatile precursors.<sup>7</sup> Inorganic anions which have been incorporated include  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,<sup>13</sup>  $\text{SiO}(\text{OH})_3^-$ ,<sup>14</sup> and several transition-metal complexes, including  $\text{Fe}(\text{CN})_6^{4-}$ ,<sup>13</sup>  $\text{M}(\text{EDTA})^{2-}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ ),<sup>15</sup> and nickel phthalocyaninetetrasulfonate.<sup>13</sup> The organic anions which have been incorporated into Li/Al LDHs are typically salts of aliphatic and aromatic carboxylic or sulfonic acids.<sup>16–18</sup> Recent studies into the reactions of Li/Al LDHs with organic anions have led to the observation of staging intermediates<sup>19</sup> and a high degree of selectivity leading to the separation of isomeric anions.<sup>20–22</sup>

Gibbsite<sup>23,24</sup> is one of four naturally occurring polymorphs of  $\text{Al}(\text{OH})_3$  along with bayerite,<sup>25,26</sup> nordstrandite,<sup>27,28</sup> and doyleite.<sup>29,30</sup> In each case, the  $\text{Al}(\text{OH})_3$  layers consist of nearly close-packed  $\text{OH}^-$  ions in which

\* To whom correspondence should be addressed. E-mail: amf@power.curtin.edu.au.

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**Table 1. Summary of the Diffraction and Elemental Analysis Data for the Rhombohedral Li/Al Layered Double Hydroxides**

guest	stoichiometry	interlayer separation (Å)	elemental analysis	
			obsd (%)	calcd (%)
chloride	[LiAl <sub>2</sub> (OH) <sub>6</sub> ]Cl·xH <sub>2</sub> O x ≈ 2	7.74	Li 3.05 Al 23.90	Li 2.96 Al 23.02
hydroxide	[LiAl <sub>2</sub> (OH) <sub>6</sub> ]OH·xH <sub>2</sub> O x ≈ 2	7.6	Li 3.23 Al 25.65	Li 3.21 Al 24.98
oxalate	[LiAl <sub>2</sub> (OH) <sub>6</sub> ] <sub>2</sub> [C <sub>2</sub> O <sub>4</sub> ]·xH <sub>2</sub> O x ≈ 3	8.6	Li 2.56 Al 22.89	Li 2.97 Al 23.06
malonate	[LiAl <sub>2</sub> (OH) <sub>6</sub> ] <sub>2</sub> [C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> ]·xH <sub>2</sub> O x ≈ 3	10.5	Li 2.18 Al 22.86	Li 2.88 Al 22.39
succinate	[LiAl <sub>2</sub> (OH) <sub>6</sub> ] <sub>2</sub> [C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> ]·xH <sub>2</sub> O x ≈ 4	12.1 <sup>a</sup>	Li 2.33 Al 21.43	Li 2.70 Al 21.00
fumarate	[LiAl <sub>2</sub> (OH) <sub>6</sub> ] <sub>2</sub> [ <i>trans</i> -C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> ]·xH <sub>2</sub> O x ≈ 5	12.1	Li 2.24 Al 20.18	Li 2.62 Al 20.36
maleate	[LiAl <sub>2</sub> (OH) <sub>6</sub> ] <sub>2</sub> [ <i>cis</i> -C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> ]·xH <sub>2</sub> O x ≈ 5	12.8 <sup>b</sup>	Li 2.06 Al 21.59	Li 2.62 Al 20.36

<sup>a</sup> Collapses to 10.7 Å on drying. <sup>b</sup> Collapses to 10.8 Å on drying.

the Al<sup>3+</sup> cations occupy two-thirds of the octahedral holes between alternate layers. The polytypism results from different stacking sequences for the layers. In this study, the intercalation chemistry of bayerite and nordstrandite is investigated together with the anion exchange chemistry of the resulting materials. A novel intercalation compound of bayerite has been reported previously in which reaction with phenylphosphonic acid leads to the functionalization of the hydroxide groups and the formation of Al<sub>2</sub>(O<sub>3</sub>PPh)<sub>3</sub>·4H<sub>2</sub>O.<sup>31</sup>

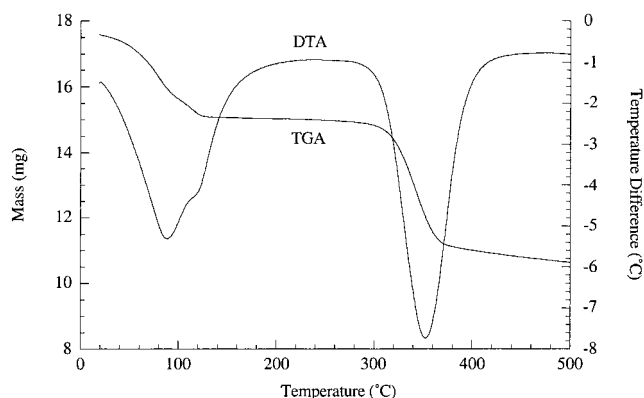
### Experimental Details

**Synthesis.** Bayerite and nordstrandite were prepared from amalgamated aluminum according to the methods reported by Thomas and Sherwood.<sup>32</sup> Intercalation was achieved by stirring a suspension of either bayerite or nordstrandite in an aqueous solution containing a 4-fold molar excess of LiCl at 90 °C overnight, giving materials with the idealized composition [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·xH<sub>2</sub>O. The samples were washed with deionized water and ethanol and left to dry in air. Subsequent anion exchange reactions of [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·xH<sub>2</sub>O were performed with a 3-fold molar excess of the disodium salt of the required dicarboxylic acid in aqueous solution at 65 °C for 24 h. In each case, complete reaction was indicated by the absence of any Bragg reflections from the host material in the powder X-ray diffraction pattern.

**Measurements.** Powder X-ray diffraction patterns were recorded on a Philips X'pert diffractometer by using Co Kα radiation. TGA/DTA measurements were recorded on a TA Instruments SDT 2960 under static air with a heating rate of 20 °C min<sup>-1</sup>. Atomic absorption analysis for Li and Al was performed on a Varian Techtron Atomic Absorption Model Spectra AA-10.

### Results and Discussion

The reaction between either bayerite or nordstrandite and lithium chloride proceeds readily under the same



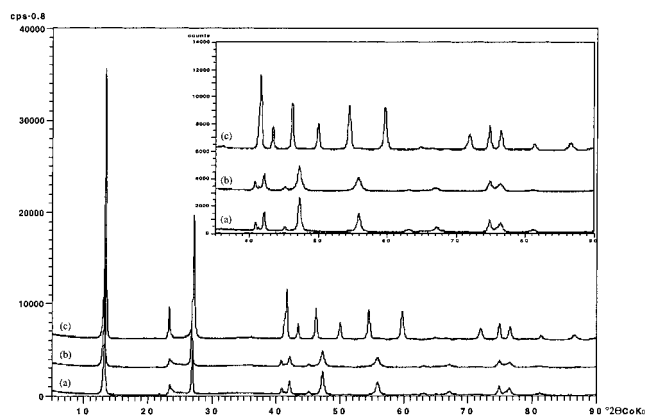
**Figure 1.** TGA and DTA curves for [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·2H<sub>2</sub>O formed from the reaction of bayerite with lithium chloride.

conditions that were used to form hexagonal [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O from gibbsite, yielding a Li/Al LDH. The composition of these materials, as determined by atomic absorption spectroscopy and TGA, showed that while the layer stoichiometry was the same, the amount of co-intercalated water was greater in the bayerite and nordstrandite derivatives, [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·2H<sub>2</sub>O, than in the gibbsite intercalation compound, [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O. The TGA trace for [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·2H<sub>2</sub>O, resulting from the intercalation of bayerite, is shown in Figure 1 and shows a 14.54% mass loss by 130 °C corresponding to the loss of two co-intercalated water molecules per formula unit to give [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl. No further mass loss is observed until 300 °C when thermal decomposition of the hydroxide layers with a mass loss of 23.50% occurs forming a material with an idealized chemical composition of Al<sub>2</sub>O<sub>3</sub>LiCl. The atomic absorption spectroscopy data is summarized in Table 1.

Powder XRD patterns of these products are shown in Figure 2, which also indicate that the same material resulted on intercalation of either bayerite or nordstrandite but that it differed from the product of the reaction with gibbsite. The diffraction pattern of the compound obtained by intercalation of either bayerite or nordstrandite was indexed using the TREOR program<sup>33</sup> to give a rhombohedral unit cell with *a* = 5.09 and *c* = 23.23 Å. Subsequent refinement of this cell gave *a* =

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**Figure 2.** Powder X-ray diffraction patterns of (a)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$  resulting from the intercalation of bayerite, (b)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$  resulting from the intercalation of nordstrandite, and (c)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot \text{H}_2\text{O}$  resulting from the intercalation of gibbsite.

**Table 2.** Observed and Calculated Bragg Reflections for  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$

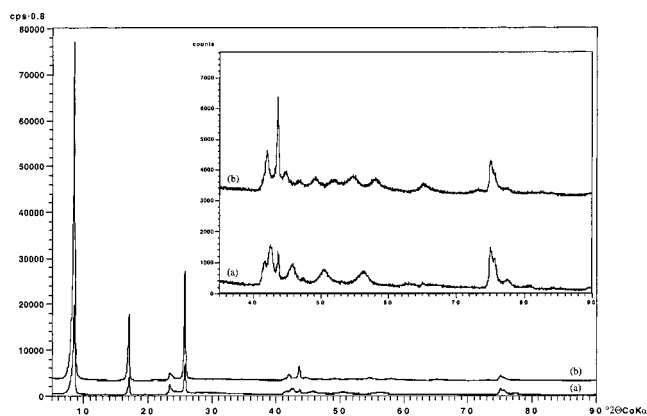
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>obsd</sub> (Å)	<i>d</i> <sub>calcd</sub> (Å) <sup>a</sup>	relative intensity (%)
0	0	3	7.7366	7.7468	100.0
1	0	0	4.4142	4.4114	11.0
0	0	6	3.8711	3.8714	44.2
0	0	9	2.5789	2.5805	7.6
1	1	1	2.5288	2.5311	4.0
1	1	2	2.4887	2.4872	14.2
1	1	4	2.3331	2.3318	4.3
1	1	5	2.2332	2.2327	23.6
1	1	8	1.9142	1.9141	13.3
1	1	10	1.7157	1.7157	2.6
1	1	11	1.6261	1.6251	4.2
3	0	0	1.4701	1.4699	9.4
3	0	3	1.4449	1.4442	7.6
3	0	6	1.3738	1.3741	2.5

<sup>a</sup> Based on a rhombohedral cell with  $a = 5.0909(5)$  and  $c = 23.217(12)$  Å.

5.0909(5) and  $c = 23.217(12)$  Å, corresponding to an interlayer separation of 7.74 Å. This interlayer separation is 0.09 Å larger than that observed in the corresponding hexagonal gibbsite intercalation compound.<sup>4</sup> This is in contrast to the pure forms of  $\text{Al}(\text{OH})_3$  where gibbsite has a larger interlayer separation than either bayerite or nordstrandite. A comparison of the observed and calculated reflections for  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$  is given in Table 2.

Repetition of the above experiments for the intercalation of  $\text{LiOH}$  instead of  $\text{LiCl}$  leads to a similar series of observations. The reactions with bayerite and nordstrandite yield a rhombohedral intercalation compound,  $[\text{LiAl}_2(\text{OH})_6]\text{OH}\cdot 2\text{H}_2\text{O}$ , with an interlayer separation of 7.6 Å, whereas the gibbsite derivative has a hexagonal unit cell. The characterizing data for this intercalation compound is summarized in Table 1.

The existence of rhombohedral  $\text{Li}/\text{Al}$  LDHs raises many questions as to whether they will show the same anion exchange behavior as the hexagonal analogues which have been shown to undergo highly selective exchange reactions with a variety of organic anions.<sup>20–22</sup> As a first step toward answering these questions, it is necessary to demonstrate the capacity of the rhombohedral  $\text{Li}/\text{Al}$  LDH for anion exchange. This has been done by investigating the exchange reactions with a



**Figure 3.** Powder X-ray diffraction patterns of (a) rhombohedral  $[\text{LiAl}_2(\text{OH})_6]_2[\text{trans-C}_4\text{H}_2\text{O}_4]\cdot 5\text{H}_2\text{O}$  and (b) hexagonal  $[\text{LiAl}_2(\text{OH})_6]_2[\text{trans-C}_4\text{H}_2\text{O}_4]\cdot 4\text{H}_2\text{O}$ .

range of dicarboxylate salts ( $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{Na}_2\text{C}_3\text{H}_2\text{O}_4$ ,  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4$ ,  $\text{Na}_2\text{-cis-C}_4\text{H}_2\text{O}_4$ , and  $\text{Na}_2\text{-trans-C}_4\text{H}_2\text{O}_4$ ). In each case, complete exchange was observed and the powder X-ray diffraction data could be fully indexed on a rhombohedral cell with  $a \approx 5.1$  Å. Powder X-ray diffraction patterns of the fumarate intercalates derived from hexagonal  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot \text{H}_2\text{O}$  and rhombohedral  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$  are shown in Figure 3 for comparison, and the diffraction and elemental analysis data are summarized in Table 1. A comparison of the diffraction data for the dicarboxylate derivatives of both forms of the initial  $\text{Li}/\text{Al}$  LDH shows that the interlayer separations are similar for the hexagonal<sup>19</sup> and rhombohedral derivatives, indicating a comparable guest loading and orientation.

One notable feature of the dicarboxylate anion exchange chemistry of hexagonal  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot \text{H}_2\text{O}$  is the formation of staging intermediates.<sup>19</sup> Reactions of rhombohedral  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$  with half and one-third stoichiometric amounts of  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4$ ,  $\text{Na}_2\text{-cis-C}_4\text{H}_2\text{O}_4$ , and  $\text{Na}_2\text{-trans-C}_4\text{H}_2\text{O}_4$  were performed in an attempt to isolate second- and third-stage intermediates, respectively. In each case, no crystalline intermediates could be isolated with the products comprised of a mixture of the host material and the first-stage product.

## Conclusions

We have synthesized a new form of  $\text{Li}/\text{Al}$  LDH,  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ , with a rhombohedral stacking sequence, by the intercalation of either the bayerite or the nordstrandite polymorphs of  $\text{Al}(\text{OH})_3$  with  $\text{LiCl}$ . This material has subsequently been shown to undergo anion exchange reactions with dicarboxylate anions but was found to differ from the previously studied hexagonal  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot \text{H}_2\text{O}$ , in that no crystalline staging intermediates could be isolated. The dicarboxylate derivatives maintained the rhombohedral structure of the host lattice.

**Supporting Information Available:** XRD data ( $d_{\text{obs}}$ ,  $I_{\text{obs}}$ , and assignment) is available for all the intercalation compounds listed in Table 1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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