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Preferential anion exchange intercalation of pyridinecarboxylate and toluate isomers in the layered double hydroxide $[LiAl_2(OH)_6]Cl \cdot H_2O$†

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All isomers of both pyridinecarboxylate (2-PA; 3-PA and 4-PA) and toluate (*o*-TA; *m*-TA and *p*-TA) can be intercalated into the layered double hydroxide $[LiAl_2(OH)_6]Cl \cdot H_2O$ in water or a water–ethanol mixture at RT to give the fully ion-exchanged first stage intercalation compounds $[LiAl_2(OH)_6] \cdot G \cdot yH_2O$ (G = 2-PA; 3-PA; 4-PA; *o*-TA; *m*-TA and *p*-TA; $y = 2.5$–3.5). Experiments also showed that using a mixed ethanol–water solvent may improve the crystallinity and decrease the production of $Al(OH)_3$. The observed interlayer separations for the intercalates vary from 14.9 Å for $[LiAl_2(OH)_6](4\text{-PA}) \cdot 3H_2O$ to 16.7 Å for $[LiAl_2(OH)_6](p\text{-TA}) \cdot 2.5H_2O$. When $[LiAl_2(OH)_6]Cl \cdot H_2O$ is added to a solution containing an equal concentration of two or three isomers of either pyridinecarboxylate or toluate anions, the host exhibits preferential anion-exchange intercalation. Following a series of competitive intercalation reactions involving two or three component mixtures we were able to determine the preference order for intercalation of both PA and TA guests in $[LiAl_2(OH)_6]Cl \cdot H_2O$. The order was found to be 4-PA > 2-PA > 3-PA and *p*-TA > *m*-TA > *o*-TA in water at both 20 and 80 °C.

Introduction

The layered double hydroxide (LDH) has been shown to undergo a wide range of facile anion exchange reactions with a variety of inorganic and organic guests.[1–6] They have been found many applications from separation chemistry to gene reservoirs.[2,4,7–20] In particular, the cation and anion ordered LDH, $[LiAl_2(OH)_6]Cl \cdot H_2O$, forms particularly crystalline intercalation compounds with a range of organic anions. Therefore, this material is most attractive as a host material for preferential exchange intercalation studies.[10,11,21–31]

In recent years we have reported preferential ion-exchange intercalation in LDHs and examined the potential of these systems for isomer separation in organic chemisty.[9–11,26,32,33] In some of our earlier studies we discovered that when equimolar mixtures of *o,m,p*-isomers of benzenedicarboxylate are added to $[LiAl_2(OH)_6]Cl \cdot H_2O$ then the "rod-like" *p*-benzenedicarboxylate (terephthalate) anion is preferentially intercalated.

In all our previous studies the organic isomers were dianions and so they were able to interact strongly with the positively charged metal-containing layers within the interlayer space. In this paper we continue to expand our studies on the number of other isomer separation systems in order to gain further insights into the factors that control the preferences expressed by layered materials. Here we report the selective intercalation of isomers of some organic mono anions, namely, pyridinecarboxylates and toluates in $[LiAl_2(OH)_6]Cl \cdot H_2O$.

Experimental

Reagents

All the starting materials used in this paper were bought from Aldrich, and have purity above 98%.

Measurements

X-Ray powder patterns were recorded from 4–100° on a Philips diffractometer using Cu Kα radiation (40 kV and 30 mA). A scan speed of 2° min^{-1} was used. TG/DTA experiments were carried out on an STA-1500, using a heating rate of 5 °C min^{-1} between 25–700 °C under static air. ^1H solution NMR spectra were recorded on a Varian Gemini spectrometer operating at 300 MHz.

Synthesis of $[LiAl_2(OH)_6]Cl \cdot H_2O$

The layered double hydroxide, $LiAl_2(OH)_6Cl \cdot H_2O$, was prepared as previously reported.[34]

Synthesis of pyridinecarboxylate intercalates

2 mmol of the appropriate pyridinecarboxylic acid was stirred with one equivalent of KOH in 5 ml of deionized water in order to prepare a solution of the potassium pyridinecarboxylate. 100 mg of $[LiAl_2(OH)_6]Cl \cdot H_2O$ was added to the solution, and the mixture was stirred for 2 hours at RT. The solid product was isolated by filtration, washed thoroughly with water and acetone, and dried.

Synthesis of toluate intercalates

The procedure is similar to that given above, but the solvent used was a 50% (v/v) solution of absolute ethanol in deionized water. 4 mmol of the appropriate toluic acid was stirred with one equivalent of KOH in 10 ml of deionized water in order to prepare a solution of the potassium toluate. 100 mg of $[LiAl_2(OH)_6]Cl \cdot H_2O$ was added to the solution, and the mixture was stirred overnight at 60 °C. The solid product was isolated by filtration, washed thoroughly with water and acetone, and dried.

A summary of the elemental microanalytical and X-ray diffraction data for all the new intercalates is presented in Table 1.

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†Electronic supplementary information (ESI) available: XRD data (I_{obs}, 2θ, assignment) for all the intercalation compounds given in Table 1. See http://www.rsc.org/suppdata/jm/b1/b102754a/

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Table 1 Summary of the elemental analysis and diffraction data

Compound	c Lattice^a/Å $d_{(002)}$/Å	Elemental analysis: obsd (calcd)^c C	H	N	Li	Al	Cl
$LiAl_2(OH)_6\cdot(2\text{-PA})\cdot0.6Al(OH)_3\cdot2.5H_2O$	$c=30.2$	19.14	4.51	3.53	1.77	18.62	0
	$d=15.1$	(19.12)	(4.49)	(3.72)	(1.84)	(18.61)	
$LiAl_2(OH)_6\cdot(3\text{-PA})\cdot0.6Al(OH)_3\cdot3.5H_2O$	$c=30.9$	18.03	4.61	3.37	1.73	17.28	0
	$d=15.5$	(18.25)	(4.80)	(3.55)	(1.76)	(17.76)	
$LiAl_2(OH)_6\cdot(4\text{-PA})\cdot0.2Al(OH)_3\cdot3H_2O$	$c=29.7$	20.31	4.49	3.81	1.87	16.43	0
	$d=14.9$	(20.32)	(4.72)	(3.95)	(1.96)	(16.74)	
$LiAl_2(OH)_6\cdot(o\text{-TA})\cdot1.4Al(OH)_3\cdot2.5H_2O$	$c=31.5$	21.02	4.94	0	1.61	20.75	0
	$d=15.8$	(21.24)	(4.95)		(1.53)	(20.28)	
$LiAl_2(OH)_6\cdot(m\text{-TA})\cdot Al(OH)_3\cdot2.5H_2O$	$c=31.8^b$	26.33	5.15	0	1.78	16.33	0
	$d=15.9$	(26.50)	(5.21)		(1.91)	(16.74)	
$LiAl_2(OH)_6\cdot(p\text{-TA})\cdot Al(OH)_3\cdot2.5H_2O$	$c=33.3$	26.03	5.18	0	1.86	17.10	0
	$d=16.7$	(25.83)	(5.18)		(1.87)	(17.19)	

^{a}Based on hexagonal cell, $\alpha=\beta=90°$, $\gamma=120°$, $a=b\approx5.1$ Å. Values were obtained from a high resolution XRD data measurement on a Siemens 5000 instrument. ^{b}There is another phase with $c=34.5$ Å. ^{c}0 means not detected.

Competitive intercalation reactions

For competitive intercalation reactions, any two or all three of the pyridinecarboxylic or toluic acids and an equivalent of KOH were dissolved in 5 ml of water (50% water–ethanol mixture for toluic acids) to prepare potassium pyridinecarboxylates or toluates. Solid $[LiAl_2(OH)_6]Cl\cdot H_2O$ was added to the solution so that the ratio of each pyridinecarboxylate or toluate to the host was 1 : 1. The reaction mixtures were typically stirred overnight at either 20 or 80 °C. They were then filtered out and dried in air.

The pyridinedicarboxylate or toluate anions could be quantitatively removed from the intercalate phases by ion exchange with Na_2CO_3. This procedure was carried out in order to determine the percentage of each isomer intercalated in the host. Typically, 100 mg of the intercalate was mixed with a 3–4 fold excess of Na_2CO_3 in 5 ml of D_2O and stirred at 80 °C overnight. The suspension was then filtered and the filtrate placed in a 5 mm ^{1}H NMR. Only the non-overlapping peaks assignable to each isomer were use to determine the percentages of each isomer present by integration of the ^{1}H NMR resonances. The results of these experiments are summarized in Tables 3–6.

Results and discussion

Both pyridinecarboxylic acid (PA) and toluic acids (TA) exist in three geometric isomer forms as shown in Fig. 1. Reaction of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with the potassium salt of each of 2-PA; 3-PA; 4-PA; *o*-TA; *m*-TA and *p*-TA in H_2O or H_2O–EtOH yields the first stage intercalation compounds $LiAl_2(OH)_6\cdot G\cdot xH_2O$ (x *ca.* 2.5–3.5; G = 2-PA; 3-PA; 4-PA; *o*-TA; *m*-TA or *p*-TA). A summary of the elemental microanalysis, thermal analysis and diffraction data for all these compounds is given in Tables 1 and 2.

The powder XRD data for each of the intercalates can be indexed on a hexagonal unit cell, the a lattice constant remains

Table 3 Percentage of each pyridinecarboxylate intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ from 1 : 1 equimolar aqueous solution at 20 °C

Mixture^a	2-PA	3-PA	4-PA
2-PA and 3-PA	59	41	—
2-PA and 4-PA	20	—	80
3-PA and 4-PA	—	5	95
All three	26	6	68

^{a}Percentage of isomer is given by reading down the columns.

Table 4 Percentage of each pyridinecarboxylate intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ from 1 : 1 equimolar aqueous solution at 80 °C

Mixture^a	2-PA	3-PA	4-PA
2-PA and 3-PA	60	40	—
2-PA and 4-PA	40	—	60
3-PA and 4-PA	—	14	86
All three	43	6	51

^{a}Percentage of isomer is given by reading down the columns.

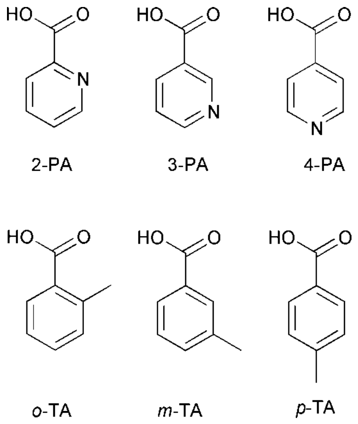

Fig. 1 Molecular structures and abbreviations used in the text of the isomers of pyridinecarboxylic acids (PA) and toluic acids (TA).

Table 2 Summary of thermal analysis (TG/DTA)^a

Intercalation Compound	Loss of Cryst. Water T/°C	Weight Loss (%)	Formation of LDO and Dehydration of $Al(OH)_3$ T/°C	Weight Loss (%)	Air Oxid. of Guest T/°C	Weight Loss (%)
$LiAl_2(OH)_6\cdot(2\text{-PA})\cdot0.6Al(OH)_3\cdot2.5H_2O$	92	13.3 (11.9)	250	28.8 (30.5)	470	60.7 (60.7)
$LiAl_2(OH)_6\cdot(3\text{-PA})\cdot0.6Al(OH)_3\cdot3.5H_2O$	92, 145	18.8 (15.9)	270	34.8 (33.7)	434, 461	63.6 (62.6)
$LiAl_2(OH)_6\cdot(4\text{-PA})\cdot0.2Al(OH)_3\cdot3H_2O$	100.3	16.2 (15.3)	289.3, 329.8	32.1 (32.0)	449.6, 474.4	63.7 (64.0)
$LiAl_2(OH)_6\cdot(o\text{-TA})\cdot1.4Al(OH)_3\cdot2.5H_2O$	89, 106	9.8 (10.0)	243, 275	31.3 (30.2)	364, 503	56.9 (58.3)
$LiAl_2(OH)_6\cdot(m\text{-TA})\cdot0.25Al(OH)_3\cdot2.5H_2O$	88	14.6 (12.4)	229	29.7 (29.2)	396, 475	64.3 (64.2)
$LiAl_2(OH)_6\cdot(p\text{-TA})\cdot0.37Al(OH)_3\cdot2.5H_2O$	131	15.7 (12.1)	254	29.6 (29.3)	420, 481	64.5 (63.4)

^{a}Weight losses, reported as observed (calculated), include all the process before the indicated process as well.

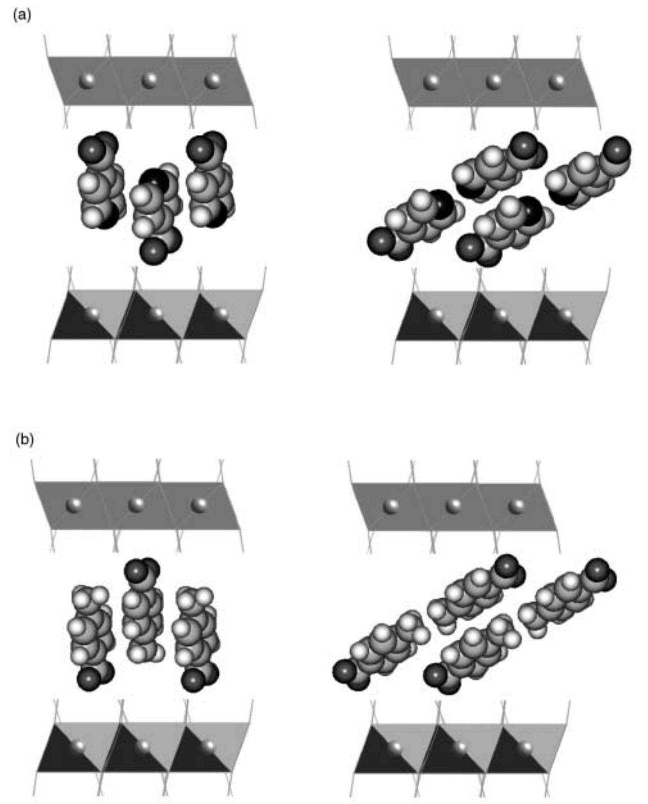

Fig. 2 Schematic representation of the possible bilayer arrangements of (a) 4-pyridinecarboxylate (4-PA) and (b) *p*-toluate (*p*-TA) anions between the $[LiAl_2(OH)_6]^+$ layers.

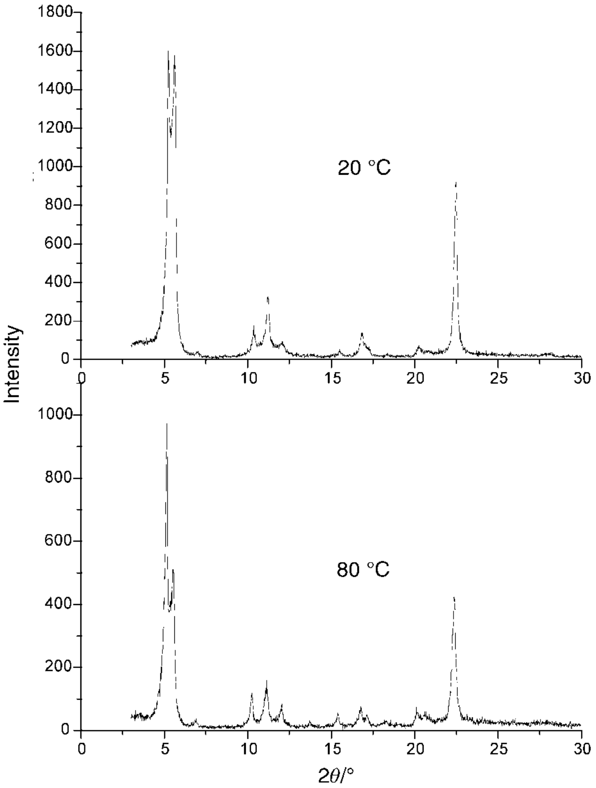

Fig. 3 Low angle region of the XRD patterns of the intercalation compounds formed by reaction of *m*-TA with $[LiAl_2(OH)_6]Cl\cdot H_2O$ at (a) 20 °C; (b) 80 °C.

invariant from the host lattice (Table 1). The interlayer separations observed with each of the guest anions take the following sequence:

p-TA (16.7Å) >*m*-TA (15.9Å) > *o*-TA (15.8Å)

4-PA (14.9Å) <2-PA (15.1Å) < 3-PA (15.5Å)

The measured interlayer separations range from 14.9–16.7 (Table 1) which are all slightly larger than the *d* spacings observed for the compounds formed by intercalation of 1,4-benzenedicarboxylate (14.2 Å)[31] or 2,5-pyridinedicarboxylate (14.0 Å) in $[LiAl_2(OH)_6]Cl\cdot H_2O$.[26] The measured interlayer separations are not sufficient for us to unambiguously determine the arrangement of the anions between the layers. We can envisage two extreme possibilities as shown in Fig. 2. The mono-anions could adopt an almost perpendicular bilayer arrangement with significant interdigitation and aromatic π–π overlap or they may adopt a non-interdigitated arrangement but are tilted at an angle of approx. 35° to the host layers. It is likely that the true situation lies somewhere between these two extremes.

Intercalation of *m*-toluate yields a biphasic mixture with each phase having a slightly different *c*-lattice constant. Fig. 3 shows the XRD patterns of a sample obtained at 20 and 80 °C. The phase with the slightly larger *d* spacing seems to be preferred at higher temperature.

In many of the intercalation compounds varying amounts of $Al(OH)_3$ (gibbsite) are observed in the XRD patterns (Fig. 4). We believe that $Al(OH)_3$ results from loss of lithium ions from the metal hydroxide layer during the intercalation reactions. This may be driven by a desire for the lattice to lower its charge density to compensate for the lower charge density in the new organic intercalate phases. The amount of $Al(OH)_3$ formed appears to decrease when the intercalation reactions are carried out in a 1 : 1 ethanol–water mixture. In addition, there seems a marked improvement in the crystallinity of the intercalation products. Transmission electron micrographs of the intercalation products (not shown) reveal that the $Al(OH)_3$ is present in the form of small gibbsite crystals rather than an $Al(OH)_3$ intergrowth within the layer structure.

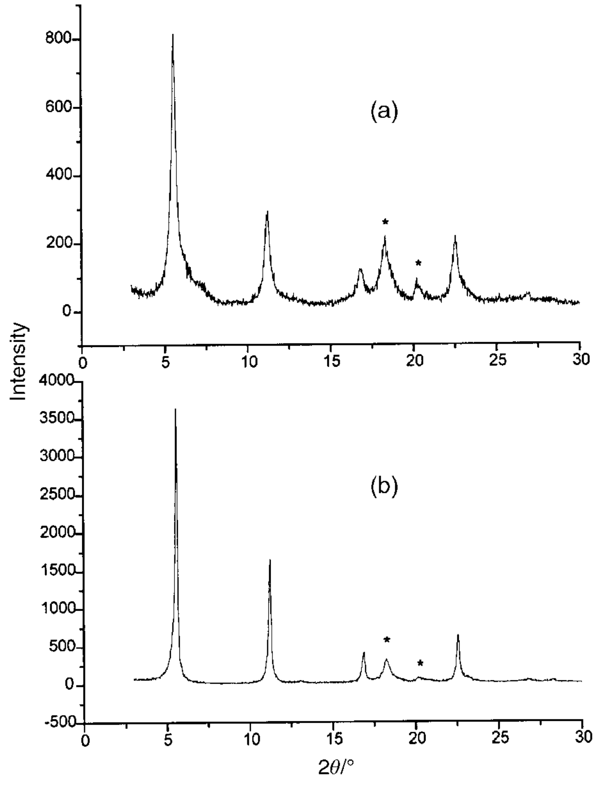

Fig. 4 The $Al(OH)_3$ impurity (peaks with *) in the intercalation product of *o*-TA in $[LiAl_2(OH)_6]Cl\cdot H_2O$ host, (a) in water solution; (b) in 50% (v/v) of ethanol–water solution.

The thermal stability of the intercalation compounds was examined by TG/DTA measurements (Table 2). The TG/DTA curves exhibit four mean regions over the temperature ranges RT–80 °C, 80–200 °C, 200–550 °C and 550–800 °C. The regions are respectively ascribed to loss of external surface water and interlamellar water molecules, dehydroxylation of metal hydroxide layers, burn of the organic anions and the final metal oxide.[35]

Preferential intercalation studies

In the earlier section we showed that all the isomers of either pyridinecarboxylate or toluate can be directly intercalated in $[LiAl_2(OH)_6]Cl \cdot H_2O$. However, we were interested in investigating whether $[LiAl_2(OH)_6]Cl \cdot H_2O$ would show any intercalation preferences for these isomeric mono-anions. The relative intercalation preferences were determined by performing competitive reactions in which multicomponent mixtures of these isomers were stirred with the host lattice at either 20 °C or 80 °C.

The percentage of each isomer intercalated in $[LiAl_2(OH)_6]Cl \cdot H_2O$ during the competition reaction was determined by solution ^{1}H NMR. When the reaction is completed, the intercalated ions (2-PA or 3-PA or 4-PA; *o*-TA or *m*-TA or *p*-TA) can be quantitatively ion-exchanged out of the solid by addition of an aqueous solution of Na_2CO_3 yielding the carbonate intercalate $[LiAl_2(OH)_6]_2 \cdot CO_3 \cdot 5H_2O$. Integration of the resonances assignable to each isomer in the ^{1}H NMR of the aqueous solution was used to confirm the selectivity of the reaction and to quantify the relative amount of intercalation for each isomer. The results of these experiments are summarized in Tables 3–6.

For example, if an aqueous solution containing a equimolar quantities of (K^+)(4-PA) and (K^+)(2-PA) is added to a suspension of $[LiAl_2(OH)_6]Cl \cdot H_2O$ in water at 20 °C then 20% of the anions intercalated are found to be 2-PA, while the preference for intercalation of 4-PA over 3-PA in $[LiAl_2(OH)_6]Cl \cdot H_2O$ at 20 °C is 95 : 5 in favour of 4-PA. Analysis of the results of all the possible binary and ternary mixtures has allowed us to construct the preference series shown below:

$$\text{4-PA} > \text{2-PA} > \text{3-PA}$$

$$p\text{-TA} > m\text{-TA} > o\text{-TA}$$

For the intercalation of 2-PA *vs.* 4-PA, 3-PA *vs.* 4-PA, and *m*-TA *vs.* *p*-TA we observe a significant difference in the anion preferences at 20 °C and 80 °C. Since our previously published studies have shown that ion-exchange intercalation in $[LiAl_2(OH)_6]Cl \cdot H_2O$ is very rapid ($t_{1/2}$ *ca.* 10 min),[27,36,37] we can assume that these reactions are under thermodynamic control. If we define an equilibrium constant $(K_{eqm}) = [\text{2-PA}_{(solution)}]/[\text{4-PA}_{(solution)}]$ for the ion-exchange intercalation reaction as shown in eqn. 1, the temperature dependence of this equilibrium constant will be directly related to the overall enthalpy of the reaction.

$$\text{4-PA}_{(solution)} + \text{2-PA}_{(intercalated)} \rightleftharpoons \text{4-PA}_{(intercalated)} + \text{2-PA}_{(solution)} \quad (1)$$

The overall enthalpy of the reaction ($\Delta H_{(reaction)}$) will be a convolution of the $\Delta H_{(solv)}$ of the two pyridinecarboxylate anions in water, the difference in the enthalpy of binding between the host and guest $\Delta H_{(host/guest)}$ and the differing guest–guest interactions $\Delta H_{(guest/guest)}$.

We were interested in identifying whether any single physical characteristic or property of these anions might be the critical factor in controlling anion intercalation preference. Our previous time-resolved, *in-situ* XRD studies lead us to believe that the isolated phases are at chemical equilibrium and that thermodynamic products are isolated. It is generally expected that the principal energy consideration is the electrostatic interaction between the carboxylate groups of the guest with the positively charged metal hydroxide layer, but it is not the only interaction we should consider, because all of the guests have only one carboxylate group, which should always be in close contact with the layers.

In order to help us address some of these issues we carried out a series of theoretical calculations using the MOPAC software within the CAChe suite.[38] We computed the dipole moment for each anion and the charge density on all the atoms for each of the six isomers. A summary of selected results of these calculations is given in Table 7.

It appears that for the anions containing one simple functional group the magnitude of the dipole moment coincides with the observed intercalation preferences. For the series of toluate isomers the order of dipole moments is the same order as the competition series:

$$p\text{-TA (11.36D)} > m\text{-TA (10.68D)} > o\text{-TA (9.11D)}$$

However, in the case of the pyridinecarboxylate isomers, which contain two functional groups, it is not sufficient to consider the magnitude of the dipole in isolation. The MOPAC calculations indicate that there is significant negative charge on the oxygen atoms of the carboxylate group and also the nitrogen atom. In the case of 4-PA, which has the highest preference, we believe that the most powerful interaction comes from its orientation of the negative charge distribution. The more "rod-like" negative charge structure means that it will be able to most effectively interact with the positively charge metal hydroxide layers.

Table 5 Percentage of each toluate intercalated in $[LiAl_2(OH)_6]Cl \cdot H_2O$ from 1 : 1 equimolar aqueous solution at 20 °C

Mixture[a]	*o*-TA	*m*-TA	*p*-TA
o-TA and *m*-TA	19	81	—
o-TA and *p*-TA	4	—	96
m-TA and *p*-TA	—	6	94
All three	5	12	83

[a]Percentage of isomer is given by reading down the columns.

Table 6 Percentage of each toluate intercalated in $[LiAl_2(OH)_6]Cl \cdot H_2O$ from 1 : 1 equimolar aqueous solution at 80 °C

Mixture[a]	*o*-TA	*m*-TA	*p*-TA
o-TA and *m*-TA	17	83	—
o-TA and *p*-TA	4	—	96
m-TA and *p*-TA	—	24	76
All three	6	33	61

[a]Percentage of isomer is given by reading down the columns.

Table 7 Calculated dipole moments and charges on nitrogen and oxygen atoms

Anion	Dipole moments/D	Calculated Charges		
		Nitrogen	Oxygen 1	Oxygen 2
2-PA	9.80	−0.116	−0.520	−0.572
3-PA	8.51	−0.182	−0.562	−0.565
4-PA	7.46	−0.181	−0.561	−0.561
o-TA	9.11		−0.570	−0.566
m-TA	10.68		−0.568	−0.569
p-TA	11.36		−0.568	−0.569

Conclusions

Pyridinecarboxylate and toluate isomers can be intercalated into the double hydroxide host, $[LiAl_2(OH)_6]Cl \cdot H_2O$, at RT. The host shows a sequential series of intercalation preferences for these anions in aqueous or ethanol–water solution. The intercalation preference order for the pyridinecarboxylates is 4-PA > 2-PA > 3-PA, while that for the toluates is *p*-TA > *m*-TA > *o*-TA.

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