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Efficient separation of pyridinedicarboxylates by preferential anion exchange intercalation in $[LiAl_2(OH)_6]Cl\cdot H_2O$†

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All six isomers of pyridinedicarboxylate (2,3-PDA; 2,4-PDA; 2,5-PDA; 2,6-PDA; 3,4-PDA; 3,5-PDA) can be intercalated by the layered double hydroxide $[LiAl_2(OH)_6]Cl\cdot H_2O$ in water at 100 °C to give the fully ion-exchanged first stage intercalation compounds $[LiAl_2(OH)_6]G_{0.5}\cdot xH_2O$ (G = 2,3-PDA; 2,4-PDA; 2,5-PDA; 2,6-PDA; 3,4-PDA; 3,5-PDA; $x = 2$–3.5) . The observed interlayer separations for the intercalates vary from 10.9 Å for the high temperature form of $[LiAl_2(OH)_6](3,5\text{-PDA})_{0.5}\cdot 2H_2O$ to 14.8 Å for $[LiAl_2(OH)_6](2,3\text{-PDA})_{0.5}\cdot 3H_2O$. When a solution containing an equal concentration of two or more of the pyridinedicarboxylate anions is added to a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ in water then the host exhibits preferential anion-exchange intercalation. Following an extensive series of competitive intercalation reactions involving two component through to six component mixtures we were able to determine the preference order for intercalation of all six PDA guests in $[LiAl_2(OH)_6]Cl\cdot H_2O$. The order was found to be 2,5-PDA > 2,3-PDA > 2,4-PDA > 2,6-PDA ≈ 3,5-PDA ≈ 3,4-PDA in water at 100 °C.

Introduction

Intercalation of guests into lamellar materials has been found to be an effective low temperature method to modify materials controllably.[1–4] It is also important in areas such as sensing, catalysis[5,6] and molecular recognition.[7,8]

In recent years we have been interested in the application of preferential intercalation in layered materials as a novel, cost effective and environmentally friendly separation science. We have found that many factors can influence the selectivity of the intercalation reaction, including temperature, shape of guest, charge density of guest and the host layers.[9] The competition between the energetics of guest solvation in the solution phase *versus* the energetics of guest–guest and guest–host interactions in the solid are key factors.

Layered double hydroxides (LDH's) can be represented by the general formula: $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2][A^{n-}_{(x/n)}]\cdot zH_2O$, where M^{II} and M^{III} are di- and tri-valent metal cations, respectively, that occupy octahedral positions in hydroxide layers. The value of x $[x = M^{III}/(M^{II} + M^{III})]$ ranges between 0.20 and 0.33 for the MgAl–LDH system[10] and A^{n-} is the interlayer charge-compensating anion, such as CO_3^{2-}, NO_3^{-}, Cl^{-}, *etc.* A large number of LDH's with a wide variety of M^{II}–M^{III} cation pairs (*e.g.*, Ca–Al) as well as M^{I}–M^{III} cation pair (*e.g.*, Li–Al) with different anions in the interlayer and their physicochemical properties have been reported.[11,12] LDH's exhibit a wide range of anion-exchange reactions with guests such as organic acids,[13,14] sulfonates,[15,16] and a range of metal complexes.[17–19]

In particular, the layered double hydroxide $[LiAl_2(OH)_6]Cl\cdot H_2O$ has been shown to undergo a wide range of facile anion-exchange reactions with a variety of inorganic and organic guests.[20–23] For example, we have reported that when $[LiAl_2(OH)_6]Cl\cdot H_2O$ is treated with pure samples of the disodium salts of either 1,2-, 1,3- or 1,4-dibenzoic acid then first stage intercalates are formed rapidly.[24] In these earlier studies we also discovered that when equimolar mixtures of all three aromatic dicarboxylate dianions are added to $[LiAl_2(OH)_6]Cl\cdot H_2O$ then the only crystalline phase observed by powder X-ray diffraction is the phase formed on intercalation of the 1,4-dibenzoate anions. In addition, the preferentially intercalated ions can be quantitatively recovered from the host.

The pyridinedicarboxylic acids are commonly used as ligands in coordination chemistry[25] and a number of the isomers have potent biological activity. For example, both 2,4-PDA and 2,5-PDA are potent inhibitors of purified prolyl 4-hydroxylase.[26] Sodium 2,6-pyridinedicarboxylate (dipicolinate) has been investigated for its inactivation of bovine carbonic anhydrase.[27] A range of 3,5-PDA derivatives exhibit substantial calcium channel antagonist activity.[28]

In order to develop a greater understanding of the factors influencing the preferences exhibited by these hosts and to widen the portfolio of guests that can be separated by this host lattice we have investigated in the present paper the intercalation of pyridinedicarboxylate anions in $[LiAl_2(OH)_6]Cl\cdot H_2O$.

Experimental details

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

The layered double hydroxide $[LiAl_2(OH)_6]Cl\cdot H_2O$ was prepared as previously reported by us.[29] A suspension of the gibbsite [γ-$Al(OH)_3$] (*ca.* 0.6 g) in water was stirred with a four fold molar excess of LiCl at 90 °C for 6 h. The solid was then isolated by filtration and washed with 5 × 10 ml of deionized water, dried in a oven at 90 °C for 1–2 h to give samples of idealized composition $[LiAl_2(OH)_6]Cl\cdot H_2O$. Elemental analysis: found (calc) for $[LiAl_2(OH)_6]Cl\cdot 0.85H_2O$ Al 22.23 (22.84); Li 3.15 (3.38); Cl 17.28 (17.25)%.

Synthesis of pyridinedicarboxylate intercalates

3 mmol of the appropriate pyridinedicarboxylic acid was stirred with one equivalent of KOH in 5 ml of deionized water in order to prepare a solution of the dipotassium pyridinedicarboxylate. 150 mg of $[LiAl_2(OH)_6]Cl\cdot H_2O$ was

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†Supplementary material: XRD data (*hkl*, *d*(Å), 2θ) for the intercalation compounds given in Table 1. Available from BLDSC (SUPP. NO. 57705, 4 pp.) or the RSC library. See Information for Authors 2000, Issue 1 (http://www.rsc.org/materials).

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Table 1 Summary of the elemental analysis and diffraction data

Guest	Number of cocryst. water, x^a	c lattice^b/Å $d_{(002)}$/Å	Elemental analysis/obsd (calcd)		
			H	C	N
2,3-PDA	3.0	$c=29.6$ $d=14.8$	4.30(4.54)	15.67(14.03)	2.50(2.34)
2,4-PDA	2.5	$c=24.4$ $d=12.2$	3.98(4.33)	14.95(14.31)	2.42(2.41)
2,5-PDA	3.5	$c=28.0$ $d=14.0$	4.33(4.74)	14.33(13.62)	2.33(2.27)
2,6-PDA	2.5	$c=29.4$ $d=14.7$	4.30(4.34)	14.70(14.47)	2.32(2.41)
3,4-PDA	3.0	$c=23.0$ $d=11.5$	4.21(4.54)	12.91(14.03)	2.03(2.34)
3,5-PDA	2.0	$c=21.8$ $d=10.9$	3.87(4.12)	15.13(14.93)	2.41(2.49)

[a] Stoichiometry based on $[LiAl_2(OH)_6]G_{0.5}\cdot x\cdot H_2O$. [b] Based on hexagonal cell, $\alpha=\beta=90°$, $\gamma=120°$, $a=b\approx5.1$ Å. Values were obtained from high resolution XRD data measurement on a Philips instrument.

added to the solution, and the mixture was stirred overnight at RT, 60, 80 or 100 °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.

Competitive intercalation reactions

For two component competitive intercalation reactions, any two of the pyridinedicarboxylic acids and KOH in the molar ratio 1 : 1 : 4 were dissolved in 10 ml of water. $[LiAl_2(OH)_6]Cl\cdot H_2O$ was added so that the pyridinedicarboxylates were in 2–3 times molar excess. The reaction mixtures were typically stirred overnight at either 60 or 100 °C. For multiple competition intercalation reactions, the potassium pyridinedicarboxylates were prepared as before and then added to the host and stirred overnight in water at either 60 or 100 °C. The solid intercalate phases were recovered by filtration and dried as before.

The pyridinedicarboxylate anions could be removed from the intercalate phases by ion-exchange with Na_2CO_3 in order to determine the percentage of each isomer that was intercalated. Typically, 150 mg of the intercalates was mixed with a 3 to 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 ^1H NMR tube.

Reagents

All the starting materials used in this paper were bought from Aldrich, with purities above 98%.

Measurements

X-Ray powder patterns were recorded from 4–60° on a Philips PW1710 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. Infrared spectra of samples in a KBr disc were recorded on a Mattison Instruments Galaxy Series 6020 spectrometer in the range 400–4000 cm^{-1}.

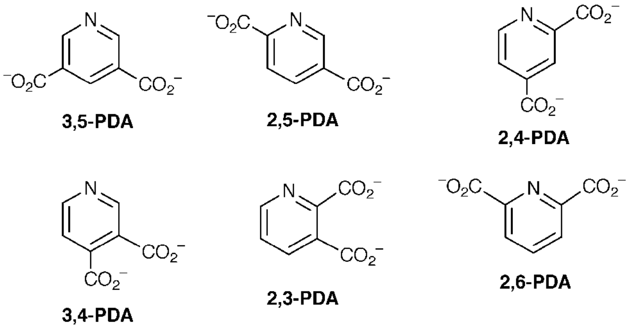

Fig. 1 Molecular structure of the six isomers of pyridinedicarboxylate.

Results and discussion

Reaction of $[LiAl_2(OH)_6]Cl\cdot H_2O$ with any one of the dipotassium salts of 2,5-PDA, 2,3-PDA, 2,4-PDA, 2,6-PDA, 3,5-PDA and 3,4-PDA (Fig. 1) in H_2O at 100 °C yields the 1st stage intercalation compounds $[LiAl_2(OH)_6]G_{0.5}\cdot xH_2O$ (x *ca.* 2–3.5; G = 2,3-PDA; 2,4-PDA; 2,5-PDA; 2,6-PDA; 3,4-PDA; 3,5-PDA), respectively. A summary of the elemental microanalytical, thermal analysis and diffraction data for all these compounds are given in Tables 1 and 2.

The powder XRD data for each of the intercalates can be indexed on a hexagonal unit. The a lattice constant remains invariant from the host lattice (Table 1). The observed interlayer separations for the intercalates vary from 10.9 Å for $[LiAl_2(OH)_6](3,5\text{-PDA})_{0.5}\cdot 3H_2O$ up to 14.8 Å for $[LiAl_2(OH)_6](2,3\text{-PDA})_{0.5}\cdot 3H_2O$. However, the powder XRD data are not of sufficiently high quality to allow us to carry out structure determination. However, by using the estimated dimensions of the guest ions we have attempted to infer the

Table 2 Summary of thermal analysis (TG/DTA)

Intercalation compounds	Loss of cryst. water		Formation of LDO		Air oxid. of guest	
	Temp./°C	Weight loss (%)	Temp./°C	Weight Loss (%)	Temp./°C	Weight loss (%)
$[LiAl_2(OH)_6](2,3\text{-PDA})_{0.5}\cdot 3.0H_2O$	95	17.5(18.0)	340	17.5(18.0)	418, 476	28.0(24.9)
$[LiAl_2(OH)_6](2,4\text{-PDA})_{0.5}\cdot 2.5H_2O$	80	16.5(15.5)	250, 300	16.5(18.6)	500	25.0(25.6)
$[LiAl_2(OH)_6](2,5\text{-PDA})_{0.5}\cdot 3.5H_2O$	80, 130	20.0(20.4)	260, 320	16.5(16.0)	510	26.0(24.1)
$[LiAl_2(OH)_6](2,6\text{-PDA})_{0.5}\cdot 2.5H_2O$	70	17.0(15.5)	255, 310	15.0(18.6)	460, 470	26.0(25.6)
$[LiAl_2(OH)_6](3,4\text{-PDA})_{0.5}\cdot 3.0H_2O$	70	17.0(18.0)	260, 323	19.0(18.0)	490	22.0(24.9)
$[LiAl_2(OH)_6](3,5\text{-PDA})_{0.5}\cdot 2.0H_2O$	120	11.0(12.8)	250, 305	21.0(19.2)	540	25.0(26.4)

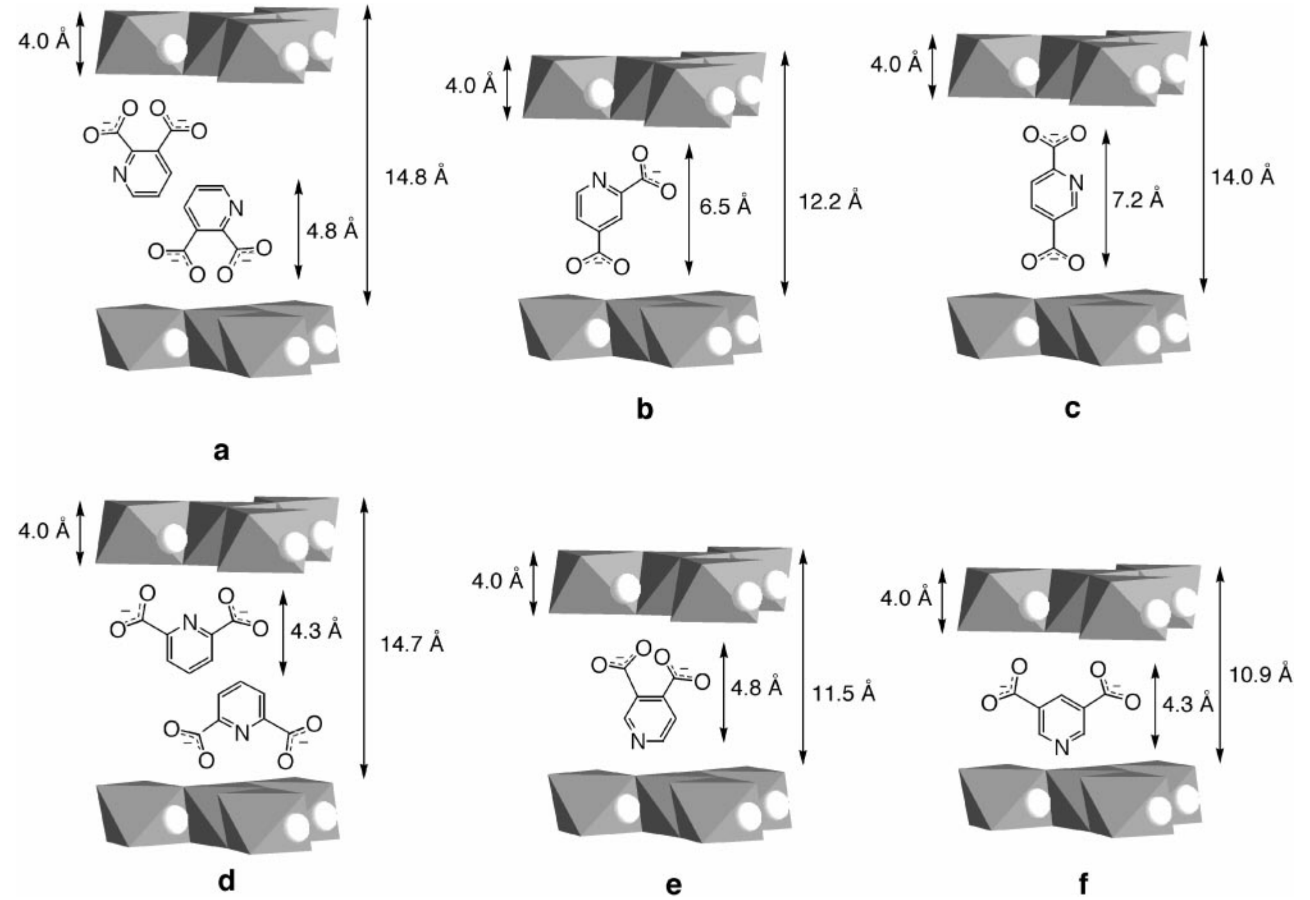

Fig. 2 Schematic illustration of the proposed orientation of the pyridinedicarboxylate anions between the $[LiAl_2(OH)_6]^+$ layers prepared at 100 °C for (a) $[LiAl_2(OH)_6](2,3\text{-PDA})_{0.5}\cdot 3H_2O$; (b) $[LiAl_2(OH)_6](2,4\text{-PDA})_{0.5}\cdot 2.5H_2O$; (c) $[LiAl_2(OH)_6](2,5\text{-PDA})_{0.5}\cdot 3.5H_2O$; (d) $[LiAl_2(OH)_6](2,6\text{-PDA})_{0.5}\cdot 2.5H_2O$; (e) $[LiAl_2(OH)_6](3,4\text{-PDA})_{0.5}\cdot 3H_2O$; (f) $[LiAl_2(OH)_6](3,5\text{-PDA})_{0.5}\cdot 3H_2O$.

orientation of the pyridinedicarboxylate guests from the observed interlayer separations. The proposed orientations of the guest ions between the $[LiAl_2(OH)_6]^+$ layers are illustrated schematically in Fig. 2. However, we cannot rule out the possibility that the guests are disordered within the layers. This is more likely to be the case for intercalates with the largest interlayer spacings.

For almost all the intercalates the interlayer separation is consistent with a monolayer of guest ions between the metal hydroxide layers. In this arrangement the carboxylate functional groups maximize their electrostatic interaction with the positively-charged layers which is likely to be the dominant energy term in controlling the guest orientation.

The intercalation of 3,4-PDA at 60 °C yields an intercalate with an interlayer separation of 14.7 Å. If the reaction is performed at 100 °C some of this phase is still present but the major phase is now a 3,4-PDA intercalate with a much reduced interlayer spacing of 11.5 Å (Fig. 3). The interlayer separation is clearly linked to the degree of hydration as the layers swell on soaking the lower *d*-spacing material in water. Dehydration

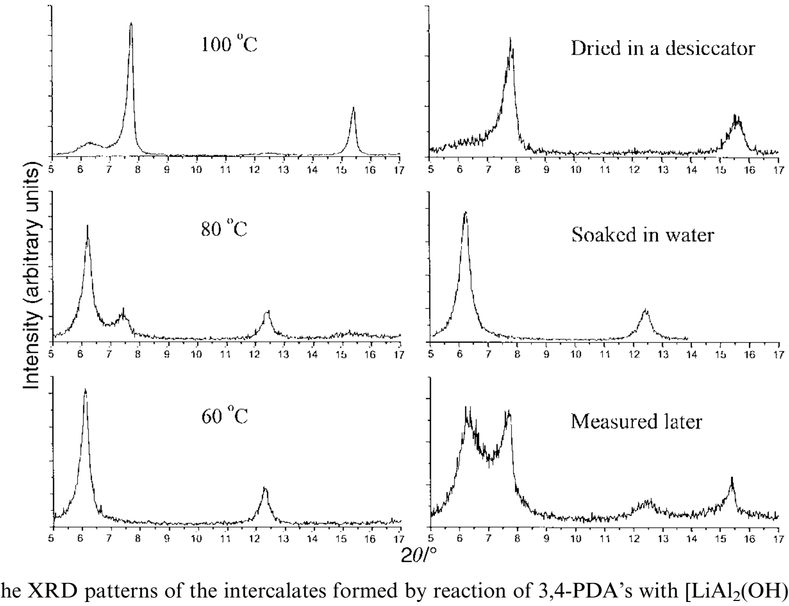

Fig. 3 Low angle region of the XRD patterns of the intercalates formed by reaction of 3,4-PDA's with $[LiAl_2(OH)_6]Cl\cdot H_2O$ at 60, 80 and 100°C. Low angle region of the XRD patterns of the intercalates XRD patterns of compound after being treated as indicated.

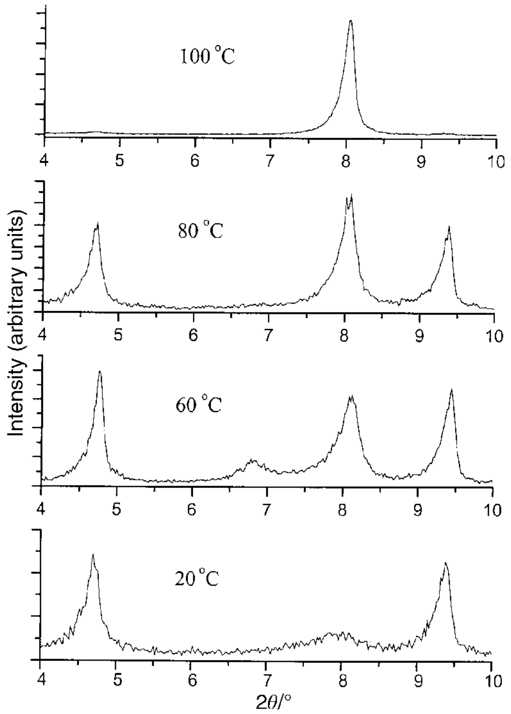

Fig. 4 Low angle region of the XRD patterns of the intercalates formed by reaction of 3,5-PDA's with $[LiAl_2(OH)_6]Cl\cdot H_2O$ at 20, 60, 80 and 100 °C.

collapses the layers back to 11.5 Å. It is likely that this process is simply the reversible co-intercalation of water, however, it may also be possible that the orientation of the 3,4-pyridinedicarboxylate within the layers changes as a function of the degree of hydration. Similar behavior has been previously observed for the intercalation of pyridine in TaS_2.[30]

The interlayer separations measured for both $[LiAl_2(OH)_6](2,3\text{-PDA})_{0.5}\cdot 5H_2O$ and $[LiAl_2(OH)_6](2,6\text{-PDA})_{0.5}\cdot 5H_2O$ are consistent with a bilayer of guest ions. However, the observed interlayer separation for both phases indicates that there must be significant π–π overlap of the pyridine ring (Fig. 2). We have previously observed a bilayer guest structure for the intercalation of the fumarate anion in $[LiAl_2(OH)_6]Cl\cdot H_2O$.[24]

When the intercalation of 3,5-PDA in $[LiAl_2(OH)_6]Cl\cdot H_2O$ is performed below 100 °C a number of other phases can be identified. The powder XRD data of the solids isolated by reaction of 3,5-PDA with $[LiAl_2(OH)_6]Cl\cdot H_2O$ in water at a number of different temperatures are shown in Fig. 4.

At room temperature the intercalation reaction does not proceed to completion, the solid product contains $[LiAl_2(OH)_6]Cl\cdot H_2O$, in addition to another poorly crystalline phase which exhibits Bragg reflections corresponding to the *d*-spacing 18.87, 11.21 and 9.41 Å (Fig. 4). These reflections can be indexed on a hexagonal unit cell with an interlayer repeat distance of 18.5 Å. Elemental microanalytical data indicates that this phase is fully ion-exchanged therefore we can rule out the possibility that is a 2nd or higher stage intercalate. The interlayer separation is sufficiently large to accommodate a bilayer of 3,5-PDA ions as shown schematically in Fig. 5. At 60 °C the XRD suggests that there are three phases present. The low temperature phase ($c = 18.5$ Å), the high temperature phase ($c = 10.9$ Å) and what we believe to be a solvated phase, shown schematically in Fig. 5, with an intermediate interlayer separation of 13.0 Å. At 80 °C the XRD of the products suggests that it now contains a higher proportion of the high temperature phase and at 100 °C this is the exclusive product.

Table 3 Percentage of each pyridinedicarboxylate intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ from 1 : 1 equimolar aqueous solution at 60 °C

Isomer[a]	2,5-PDA	2,3-PDA	2,4-PDA	2,6-PDA	3,5-PDA	3,4-PDA
2,5-PDA		25.8	2.4	9.4	4.5	0.9
2,3-PDA	74.2		17.1	10.0	5.4	11.9
2,4-PDA	97.6	82.9		15.6	58.3	10.2
2,6-PDA	90.6	90.0	84.4		28.4	26.0
3,5-PDA	95.5	94.6	41.7	71.6		1.9
3,4-PDA	99.1	88.				

[a] The percentage of each isomer that is intercalated is given by reading down the columns.

Temperature programmed thermal analysis experiments have been performed on all the new intercalate phases. All the thermogravimetric and differential thermal analysis (TG/DTA) experiments support the composition suggested by the elemental microanalytical data. The results are summarized in Table 2. All the intercalates exhibit three stages of weight loss. Initially, each sample loses co-intercalated water up to *ca.* 100 °C. There is a further weight loss around 300 °C to form a layered double oxide (LDO) phase. Above 400 °C, the pyrolysis and oxidation of the organic guest occur, which gives rise to two exothermic peaks in the DTA and subsequent formation of lithium and aluminium oxides.

Preferential intercalation studies

We have previously shown that $[LiAl_2(OH)_6]Cl\cdot H_2O$ can preferentially intercalate maleate ions from an aqueous solution containing an equimolar mixture of maleate and fumarate. More recently, we have shown that the terephthalate anion can be intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ with a >98% selectivity from an aqueous solution containing an equimolar mixture of terephthalate, isophthalate and phthalate anions.[9,24,31]

In the earlier section we reported that all six isomers of pyridinedicarboxylate can be intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$. Therefore we were interested to investigate if $[LiAl_2(OH)_6]Cl\cdot H_2O$ would show any intercalation preferences for the six isomeric anions. The relative intercala-

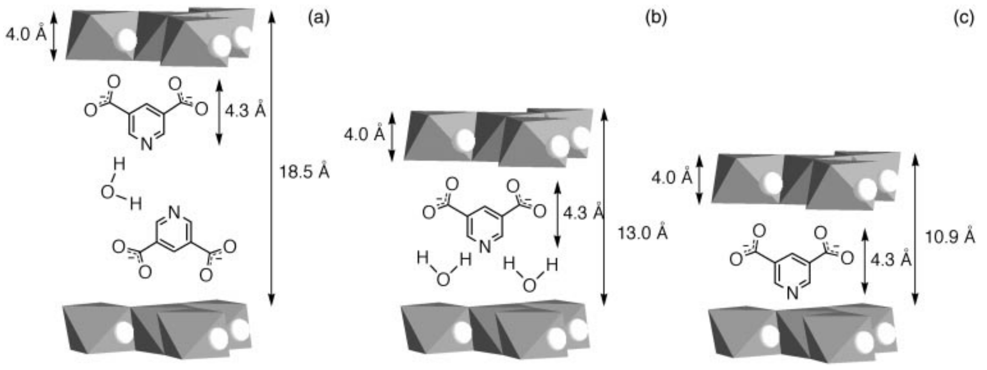

Fig. 5 Schematic illustration of the proposed orientation of the 3,5-pyridinedicarboxylate anions between the $[LiAl_2(OH)_6]^+$ layers for (a) product formed at 20, (b) 60 and (c) 100 °C.

Table 4 Percentage of each pyridinedicarboxylate intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ from 1 : 1 equimolar aqueous solution at 100 °C

Isomer[a]	2,5-PDA	2,3-PDA	2,4-PDA	2,6-PDA	3,5-PDA	3,4-PDA
2,5-PDA		6.4	0.9	0.4	6.8	1.1
2,3-PDA	93.6		15.1	0.0	4.0	11.3
2,4-PDA	99.1	84.9		6.5	50.2	13.3
2,6-PDA	99.6	100.0	93.5		34.8	16.1
3,5-PDA	93.2	96.0	49.8	65.2		2.9
3,4-PDA	98.9	88.7	86.7	83.9	97.1	

[a] The percentage of each isomer intercalated is given by reading down the columns.

tion preferences were determined by performing numerous competitive reactions in which multicomponent mixture of the 6 isomers were stirred with an excess of the host lattice at 60 and 100 °C.

The percentage of each isomer intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ during these competition reactions was determined by carbonate exchange followed by solution ^1H NMR. Integration of the non-overlapping resonances assignable to each isomer was used to determine the relative amounts of intercalation for each isomer. The results of these experiments are summarized in Tables 3 and 4. Analysis of the results of the 15 possible binary mixtures has allowed us to construct the preference series shown below:

$$\begin{aligned} &2,5\text{-PDA} > 2,3\text{-PDA} > 2,4\text{-PDA} > 2,6\text{-PDA} \\ &> 3,5\text{-PDA} > 3,4\text{-PDA} \end{aligned} \qquad (1)$$

For example, if an aqueous solution containing equimolar quantities of $(K^+)_2$(3,4-PDA) and $(K^+)_2$(2,5-PDA) is added to a suspension of $[LiAl_2(OH)_6]Cl\cdot H_2O$ in water at 60 °C then 99.1% of the anions intercalated are found to be 2,5-PDA. Separation of $(K^+)_2$(3,5-PDA) from $(K^+)_2$(3,4-PDA) is equally dramatic with 98.1% of the 3,5-PDA ions being intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ in the presence of an equimolar amount of $(K^+)_2$(3,4-PDA).

Clearly with six different isomers a huge number of different multicomponent mixtures can be prepared. However, we were interested to investigate the intercalation selectivity for a number of multicomponent mixtures to see if the preference order derived from the binary experiments still operated for more complex mixtures.

The outcome of the intercalation experiment performed with an aqueous solution containing an equimolar mixture of all six anions showed that at 60 °C more than 50% of the intercalated anions are 2,5-PDA (see Table 5). At 100 °C this preference is slightly more (see Table 6. The next most preferred anion is 2,3-PDA and both 2,5-PDA and 2,3-PDA account for over 76% of the intercalated anions which are extracted from this aqueous mixture at 100 °C. The order for the four remaining lesser preferred anions was studied in more detail by preparing a four component mixture and four three component mixtures without the 2,5-PDA and 2,3-PDA isomers.

We were most interested to determine what the critical factors controlling anion preferences are. Previously, we have shown using time-resolved *in situ* X-ray diffraction studies that ion-exchange intercalation in $[LiAl_2(OH)_6]Cl\cdot H_2O$ is very rapid ($t_{1/2}$ *ca.* 10 min) and that the observed phases are the thermodynamically favored products at the temperature of the reaction.[32] It is expected that the principal energy consideration is the electrostatic interaction between the carboxylate groups in the guest with the positively charged metal hydroxide layer. Surprisingly, the observed preference is not related to the guest that produces the smallest interlayer expansion on intercalation.

In order to help us address some of these issues affecting the observed selectivities we have performed a series of semiempirical quantum chemical calculations on the guest ions using the AM1 method within the Hyperchem program.[17] We were able to compute the polarity for each anion and the charge density on the oxygens of each of the carboxylate groups for each of the six isomers. A summary of the results of these calculations is given in Table 7.

The observation that 2,5-PDA is by far the most preferred guest of the six different anions studied is consistent with our previously reported preferences for other families of isomeric dicarboxylates.[9,24,31] We believe that the more linear, rod-like dicarboxylates are able to interact most strongly with both cationic metal hydroxide layers, since all negatively charged oxygen atoms in this isomer are in closest contact with the positively charged layers. The preferences expressed for the remaining 5 isomers is much more difficult to rationalise. 2,3-PDA is the next most highly favoured anion. The angle between the carboxylate groups for this isomer is now only 60° whereas three other isomers have 120° angles between their carboxylate groups. However, our calculations shows that this isomer has the largest dipole moment of all the isomers and so by forming a bilayer of guest ions within the layers it is able to form the next most thermodynamically stable phase. For the remaining four isomers the factors which control the specific

Table 5 Percentage of each isomer intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ from an aqueous solution containing equimolar amounts of the potassium salts of pyridinedicarboxylates at 60 °C

Isomer mixture	2,5-PDA	2,3-PDA	2,4-PDA	2,6-PDA	3,5-PDA	3,4-PDA
All 6 isomers	50.5	33.5	9.5	1.2	2.0	3.3
5 isomers without 2,5-PDA	—	50.9	19.4	10.8	8.3	10.6
4 isomers without 2,5-PDA, 2,3-PDA	—	—	63.0	3.9	28.7	4.4
3 isomers: 2,6-PDA, 3,5-PDA, 3,4-PDA	—	—	—	42.0	45.2	12.8
3 isomers: 2,4-PDA, 3,5-PDA, 3,4-PDA	—	—	62.1	—	31.4	6.5
3 isomers: 2,4-PDA, 2,6-PDA, 3,4-PDA	—	—	54.7	13.0	—	32.3
3 isomers: 2,4-PDA, 2,6-PDA, 3,5-PDA	—	—	50.5	5.2	44.3	—

Table 6 Percentage of each isomer intercalated in $[LiAl_2(OH)_6]Cl\cdot H_2O$ from an aqueous solution containing equimolar amounts of the potassium salts of pyridinedicarboxylates at 100 °C

Isomer mixture	2,5-PDA	2,3-PDA	2,4-PDA	2,6-PDA	3,5-PDA	3,4-PDA
All 6 isomers	58.6	23.8	8.1	3.6	2.2	3.7
5 isomers without 2,5-PDA	—	62.2	19.1	6.4	3.1	9.2
4 isomers without 2,5-PDA, 2,3-PDA	—	—	60.8	4.8	23.7	10.7
3 isomers: 2,6-PDA, 3,5-PDA, 3,4-PDA,	—	—	—	38.4	45.8	15.8
3 isomers: 2,4-PDA, 3,5-PDA, 3,4-PDA,	—	—	60.6	—	28.5	10.8
3 isomers: 2,4-PDA, 2,6-PDA, 3,4-PDA,	—	—	60.8	11.3	—	27.8
3 isomers: 2,4-PDA, 2,6-PDA, 3,5-PDA,	—	—	47.0	10.5	42.5	—

Table 7 Calculated dipole moments and charges for the pyridinedicarboxylates

		Calculated charges				
Anions	Dipole moments/D	Nitrogen	Oxygen 1	Oxygen 2	Oxygen 3	Oxygen 4
2,3-PDA	10.05	–0.15	–0.60	–0.49	–0.48	–0.66
2,4-PDA	5.92	–0.14	–0.57	–0.58	–0.57	–0.61
2,5-PDA	1.54	–0.15	–0.56	–0.60	–0.60	–0.60
2,6-PDA	7.93	–0.08	–0.54	–0.62	–0.62	–0.54
3,4-PDA	8.73	–0.22	–0.65	–0.50	–0.49	–0.65
3,5-PDA	4.89	–0.22	–0.61	–0.58	–0.58	–0.61

preferences appear to be much more subtle. 3,5-PDA is preferred in competition with 3,4-PDA in spite of the fact that 3,4-PDA has the higher dipole moment. Perhaps the nitrogen atom is more available in 3,5-PDA for hydrogen bonding with one of the host layers.

Conclusions

All the isomers of pyridinedicarboxylate can be intercalated successfully into the Li/Al double hydroxide host $[LiAl_2(OH)_6]Cl\cdot H_2O$ at 100 °C. The host shows a remarkable sequential series of intercalation preferences for these anions in aqueous solution. We believe the host selects anions based on their ability to interact strongly with both cationic layers and also maximize guest–guest interactions.

Consequently, $[LiAl_2(OH)_6]Cl\cdot H_2O$ exhibits the strongest affinity for 2,5-pyridinedicarboxylate both from binary mixtures of the other isomers but also from a mixture of all six isomers. The sequential nature of the selectivity suggests that this host material could be exploited as a method for the chemical separation of these anions from solution.

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