Selective anion-exchange intercalation of isomeric benzoate anions into the layered double hydroxide [LiAl$_2$(OH)$_6$]Cl·H$_2$O

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Abstract

All the geometric isomers of the benzoate derivatives, $XC_6H_4CO_2^-$ ($X = $ F, Cl, Br, OH, OCH$_3$, NO$_2$, CO$_2$CH$_3$, NH$_2$, N(CH$_3$)$_2$) can be intercalated into the layered double hydroxide [LiAl$_2$(OH)$_6$]Cl·H$_2$O in 50% (v/v) water/ethanol solution at 80 °C to give fully anion-exchanged first stage intercalation compounds [LiAl$_2$(OH)$_6$]G·yH$_2$O ($G = $ a substituted benzoate). The observed interlayer separations of the intercalates vary from 14.3 Å for [LiAl$_2$(OH)$_6$](4-nitrobenzoate)·2H$_2$O to 20.6 Å for [LiAl$_2$(OH)$_6$](3-dimethylaminobenzoate)·3H$_2$O. Competitive intercalation studies using mixtures of isomeric benzoates showed that the 4-isomers and 2-isomers are the most and the least preferred anions, respectively. Comparing the calculated dipole moments of the anions with the observed isomeric intercalation preferences suggests that dipole moment may be a good general index for the preference; however, it should be remembered that the bulkiness and electronegativity of the other substituent could be very important factors that affect the preferential intercalation.
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1. Introduction

The layered double hydroxides (LDHs), $[M_xM'_{1-x}$(OH)$_2]A_y$·mH$_2$O (where M, M' are metal ions; A is an anion) have been shown to undergo a wide range of facile anion exchange reactions [1–5]. Consequently, LDHs have been used in many applications such as syntheses of various materials [1,3,4,6,7], storage of active molecules [8,9], controlled release of drug molecules [10–12] and chemical separation processes [13–18]. Among them, [LiAl$_2$(OH)$_6$]Cl·H$_2$O is relatively stable with most anionic guests, therefore it was chosen for a some detailed preferential ion-exchange intercalation studies [13,14, 19–21].

Preferential exchange intercalation could be a possible method for isomer separation. Generally speaking, the preference could be affected by factors such as solvent, temperature, concentrations of competing anions, charge density of anions, charge density of hydroxide layers, charge distribution of anions, interaction between the intercalated anions and hydrogen bonding between anion and the hydroxide layer; however, the factors can be limited to charge distribution of anions, hydrogen bonding between anions and hydroxide layer, interaction among anions if the competition reactions of isomeric anions are carried out at given temperature in dilute solution of given concentrations [2,13,14,16–18,20–24].

In our earlier studies we have discovered that when equimolar mixtures of isomers were added to [LiAl$_2$(OH)$_6$]Cl·H$_2$O, or other LDHs such as [Ca$_2$Al(OH)$_6$]NO$_3$·H$_2$O then the rod-like anions were intercalated the most preferentially [13,18,20,21]. For example, in case of pyridinedicarboxylates (PDAs), 2,3- and 2,6-PDAs are intercalated in [LiAl$_2$(OH)$_6$] host with a double layer arrangement, while the others, 2,4-, 2,5-, 3,4- and 3,5-PDAs are arranged in a single layer in between the hydroxide layers. For the double layer intercalated 2,3- and 2,6-PDAs, the order of preference is the same as the dipole moments, which is 2,3-PDA > 2,6-PDA; for single layer intercalated 2,4-, 2,5-, 3,4- and 3,5-PDAs, the order is

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2,5-PDA > 2,4-PDA > 3,5-PDA > 3,4-PDA is the same as the order of hydrogen bond numbers, which respectively are 4 (all four oxygen atoms in 2,5-PDA anion are in close contact with the hydroxide layer) > 3 (only three oxygen atoms in 2,4-PDA could be in close contact) > 2 + 1 (two oxygen atoms and one nitrogen atom in 3,5-PDA are in close contact) > 2 (two oxygen atoms are in close contact, and one nitrogen atom in 3,4-PDA may be touched by the hydroxide layer). The complete preference series was found to be 2,5-PDA > 2,3-PDA > 2,4-PDA > 2,6-PDA > 3,5-PDA > 3,4-PDA, which could mean that hydrogen bond may be slightly more powerful than dipole moments in affecting the preference of the host [20].

Following this observation, we have synthesised and investigated the preferential intercalation of pyridinecarboxylate anions (PAs) and toluate anions (TAs) in [LiAl$_2$(OH)$_6$] host and found that the preferential orders are, for PAs, 4-PA > 2-PA > 3-PA, and for TAs, *p*-TA > *m*-TA > *o*-TA. The preference order of TAs is the same as the dipole moment order, but that is not the exact order of PAs, since the rod-like 4-PA has the smallest dipole moment while it is the most favourable anion to intercalate in the host. The experiments support that all the anions are double layered arranged in between the hydroxide layers. We suggested that the symmetrical nature of 4-PA may lead a closer contact with hydroxide layers [13].

In order to gain a greater insight into the factors that control these anion intercalation preferences we have investigated the selective intercalation of the three geometric isomeric forms of nine substituted benzoates, $XC_6H_4COO^-$, where X = F, Cl, Br, OH, OCH$_3$, NO$_2$, CO$_2$CH$_3$, NH$_2$, N(CH$_3$)$_2$ in the [LiAl$_2$(OH)$_6$]Cl·H$_2$O. These substituents span a wide range of different characteristics such as electronegativity, bulk and hydrogen bonding ability.

2. Experimental section

2.1. Regents

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

2.2. Measurements

X-ray powder patterns were recorded from 3–25° on a Philips diffractometer using Cu$K\alpha$ radiation (40 kV and 30 mA). A scan speed of 2°/min was used. ^{1}H solution NMR spectra were recorded on a Varian spectrometer operating at 300 MHz. Elemental analysis was performed by the analytical services at the Inorganic Chemistry Laboratory, Oxford.

2.3. Synthesis of [LiAl$_2$(OH)$_6$]Cl·H$_2$O

The LDH, [LiAl$_2$(OH)$_6$]Cl·H$_2$O, was prepared as reported previously [25].

2.4. Synthesis of the intercalation compounds

About 2 mmol of the appropriate acid was stirred with 2 mmol of KOH in 7 mL of 50% ethanol in deionised water (v/v) to produce a clear solution of its potassium salt. Heating or more solvent was required if the acid could not be dissolved initially. Then 150 mg of [LiAl$_2$(OH)$_6$]Cl·H$_2$O was added to the solution, and the mixture stirred for 2–7 h at 80 °C. The solid product was isolated by filtration, washed thoroughly with water and acetone, dried and analysed.

In some cases, such as the syntheses of 2- and 3-hydroxylbenzoate, 2- and 3-dimethylaminobenzoate, 2-bromobenzoate, 3-nitrobenzoate, molar ratio of guest to host was increased up to 8:1 in order to obtain fully exchanged samples.

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

2.5. Competitive intercalation reactions

For competitive intercalation reactions, any two or all three of the substituted benzoic acids and equivalent KOH (~2 mmol) were dissolved in 7 mL of 50% ethanol/water to prepare potassium salts. Again full dissolution of the acids should be achieved before the following step. [LiAl$_2$(OH)$_6$]Cl·H$_2$O was added to the solution so that each isomer and the host were equimolar. The reaction mixture was typically stirred for 7 h at 80 °C, and then the solid filtered, washed and dried in air. XRD patterns of the products were measured to assure that fully exchanged samples had been obtained. Those that had not fully exchanged were repeated using higher guest to host ratios.

The anions were removed from the intercalate phases by ion exchange with CO_3^{2-} in order to determine the percentage of each isomer that had intercalated. Typically, 100 mg of the intercalation compound was mixed with a 3–6-fold excess of Na$_2$CO$_3$ in 5 mL of D$_2$O and stirred at 80 °C overnight. The suspension was then filtered: the filtrate was placed in a 5 mm ^{1}H NMR tube and its ^{1}H NMR spectrum recorded; the XRD pattern of the solid was measured to ensure that all the original anions had been fully replaced. The non-overlapping NMR peaks assignable to each isomer were integrated. By assuming each proton on the benzene ring produces the same area of the NMR peaks, the relative amount of each isomer intercalated was estimated. The results of these experiments are summarised in Table 2.

2.6. Calculation of dipole moments

MOPAC in the CACHe package was used to carry out these calculations [26]. Some selected results were shown in Table 3.

Table 1
Composition of intercalation compounds

Guests	Formula (LA = LiAl$_2$(OH)$_6$; G = Guest)	d spacing*/Å	Composition/found (calculated)**						
			C	H	N	Li	Al	X
2-flourobenzoate (C$_7$H$_4$FO$_2$)	$LA \cdot G \cdot 0.6$Al(OH)$_3 \cdot 2$H$_2$O	15.5	21.5 (21.8)	4.0 (4.1)	0	1.7 (1.8)	18.2 (18.2)	
3-flourobenzoate (C$_7$H$_4$FO$_2$)	$LA \cdot G \cdot 0.5$Al(OH)$_3 \cdot 2$H$_2$O	15.2	21.9 (22.3)	4.3 (4.1)	0	1.8 (1.8)	17.7 (17.9)	
4-flourobenzoate (C$_7$H$_4$FO$_2$)	$LA \cdot G \cdot 0.5$Al(OH)$_3 \cdot 2$H$_2$O	15.4	22.0 (22.3)	4.2 (4.1)	0	1.8 (1.8)	17.4 (17.9)	
2-chlorobenzoate (C$_7$H$_4$ClO$_2$)	$LA \cdot G \cdot 1.3$Al(OH)$_3 \cdot 2$H$_2$O	15.6	18.2 (18.4)	3.9 (4.0)	0	1.6 (1.5)	20.2 (19.5)	8.4 (7.8)
3-chlorobenzoate (C$_7$H$_4$ClO$_2$)	$LA \cdot G \cdot 0.6$Al(OH)$_3 \cdot 3$H$_2$O · 0.5C$_2$H$_5$OH	16.5	21.6 (21.7)	4.4 (4.7)	0	1.7 (1.6)	15.9 (15.9)	8.0 (8.0)
4-chlorobenzoate (C$_7$H$_4$ClO$_2$)	$LA \cdot G \cdot 0.5$Al(OH)$_3 \cdot 2.5$H$_2$O · 0.2C$_2$H$_5$OH	16.6	21.6 (21.6)	4.6 (4.3)	0	1.7 (1.7)	16.6 (16.4)	8.6 (8.6)
2-bromobenzoate (C$_7$H$_4$BrO$_2$)	$LA \cdot G \cdot 1.2$Al(OH)$_3 \cdot 2$H$_2$O	15.4	17.2 (17.1)	3.5 (3.6)	0	1.4 (1.4)	17.4 (17.5)	16.5 (16.2)
3-bromobenzoate (C$_7$H$_4$BrO$_2$)	$LA \cdot G \cdot 0.5$Al(OH)$_3 \cdot 1.5$H$_2$O	18.0	19.5 (19.6)	4.0 (3.4)	0	1.6 (1.6)	16.0 (15.7)	19.0 (18.6)
4-bromobenzoate (C$_7$H$_4$BrO$_2$)	$LA \cdot G \cdot 0.4$Al(OH)$_3 \cdot 2$H$_2$O	17.2	19.7 (19.5)	3.9 (3.6)	0	1.6 (1.6)	15.0 (15.0)	18.4 (18.6)
2-hydroxylbenzoate (C$_7$H$_5$O$_3$)	$LA \cdot G \cdot 0.7$Al(OH)$_3 \cdot 2.5$H$_2$O	15.3	20.7 (21.0)	4.1 (4.6)	0	1.7 (1.7)	18.3 (18.2)	
3-hydroxylbenzoate (C$_7$H$_5$O$_3$)	$LA \cdot G \cdot$ Al(OH)$_3 \cdot 2.5$H$_2$O	14.9	19.76 (19.87)	5.0 (4.5)	0	1.8 (1.6)	19.3 (19.13)	
4-hydroxylbenzoate (C$_7$H$_5$O$_3$)	$LA \cdot G \cdot 0.3$Al(OH)$_3 \cdot 2$H$_2$O	15.0	23.3 (23.4)	4.5 (4.5)	0	1.9 (1.9)	17.0 (17.3)	
2-methoxybenzoate (C$_8$H$_7$O$_3$)	$LA \cdot G \cdot 0.6$Al(OH)$_3 \cdot 3$H$_2$O	18.9/17.2	22.7 (23.2)	4.7 (5.1)	0	1.7 (1.7)	17.1 (16.9)	
3-methoxybenzoate (C$_8$H$_7$O$_3$)	$LA \cdot G \cdot 0.4$Al(OH)$_3 \cdot 2.5$H$_2$O	17.9	24.5 (24.6)	5.0 (5.0)	0	1.7 (1.8)	16.2 (16.6)	
4-methoxybenzoate (C$_8$H$_7$O$_3$)	$LA \cdot G \cdot 0.3$Al(OH)$_3 \cdot 2$H$_2$O	15.3	26.0 (25.7)	4.8 (4.8)	0	1.8 (1.9)	16.8 (16.6)	
2-aminobenzoate (C$_7$H$_6$NO$_2$)	$LA \cdot G \cdot$ Al(OH)$_3 \cdot 3.5$H$_2$O	14.5	18.9 (19.1)	5.0 (5.0)	3.1 (3.2)	1.9 (1.6)	18.3 (18.4)	
3-aminobenzoate (C$_7$H$_6$NO$_2$)	$LA \cdot G \cdot 0.5$Al(OH)$_3 \cdot 1.5$H$_2$O · C$_2$H$_5$OH	18.8	26.5 (26.3)	5.8 (5.5)	3.4 (3.4)	1.7 (1.7)	16.7 (16.4)	
4-aminobenzoate (C$_7$H$_6$NO$_2$)	$LA \cdot G \cdot 0.4$Al(OH)$_3 \cdot 2$H$_2$O	15.1	22.9 (23.0)	4.9 (4.7)	3.8 (3.8)	1.9 (1.9)	17.4 (17.7)	
2-dimethylaminobenzoate (C$_9$H$_{10}$NO$_2$)	$LA \cdot G \cdot 1.9$Al(OH)$_3 \cdot 3$H$_2$O	17.9	20.5 (20.4)	5.0 (5.3)	2.6 (2.6)	1.5 (1.3)	19.5 (19.9)	
3-dimethylaminobenzoate (C$_9$H$_{10}$NO$_2$)	$LA \cdot G \cdot 0.5$Al(OH)$_3 \cdot 3$H$_2$O	20.6/19.0	25.9 (25.7)	5.3 (5.6)	3.4 (3.3)	1.6 (1.6)	16.4 (16.0)	
4-dimethylaminobenzoate (C$_9$H$_{10}$NO$_2$)	$LA \cdot G \cdot 0.2$Al(OH)$_3 \cdot 2.5$H$_2$O	17.6	28.0 (27.9)	5.2 (5.6)	3.5 (3.6)	1.7 (1.8)	15.0 (15.3)	
Monomethyl 1,2-benzenedicarboxylate (C$_9$H$_7$O$_4$)	$LA \cdot G \cdot 0.4$Al(OH)$_3 \cdot$ H$_2$O	15.4	27.2 (27.6)	4.5 (4.2)	0	1.7 (1.8)	16.9 (16.6)	
Monomethyl 1,3-benzenedicarboxylate (C$_9$H$_7$O$_4$)	$LA \cdot G \cdot 0.8$Al(OH)$_3 \cdot 2$H$_2$O	17.4	24.9 (24.5)	5.1 (4.4)	0	1.6 (1.6)	17.7 (17.2)	
Monomethyl 1,4-benzenedicarboxylate (C$_9$H$_7$O$_4$)	$LA \cdot G \cdot 0.5$Al(OH)$_3 \cdot 3$H$_2$O	18.9	24.3 (24.8)	4.7 (4.8)	0	1.7 (1.6)	15.5 (15.5)	
2-nitrobenzoate (C$_7$H$_4$NO$_3$)	$LA \cdot G \cdot 0.6$Al(OH)$_3 \cdot 2$H$_2$O	15.1	20.3 (20.4)	4.2 (3.9)	3.3 (3.4)	1.7 (1.7)	17.1 (17.0)	
3-nitrobenzoate (C$_7$H$_4$NO$_3$)	$LA \cdot G \cdot 0.33$Al(OH)$_3 \cdot 2$H$_2$O	15.9	21.2 (21.6)	4.2 (3.9)	3.5 (3.6)	1.6 (1.8)	15.6 (16.0)	
4-nitrobenzoate (C$_7$H$_4$NO$_3$)	$LA \cdot G \cdot 0.2$Al(OH)$_3 \cdot 2$H$_2$O	14.3	22.2 (22.1)	3.7 (3.9)	3.7 (3.7)	1.7 (1.8)	16.0 (15.6)	

*Based on the first two or three harmonics of its XRD pattern.

**All the compounds were analysed for Cl to make sure if all the chlorine was exchanged. X is F, Cl or Br where there is in the guest molecule.

Table 2
The percentages of the indicated component in the intercalation compounds

Compounds	Binary mixtures			Ternary mixture	
	2-isomer in a 2-/3-mixture	2-isomer in a 2-/4-mixture	3-isomer in a 3-/4-mixture	2-isomer	3-isomer
Fluorobenzoate	41.5	41.6	48.6	22.4	40.4
Chlorobenzoate	21.7	4.7	49.8	7.1	45.2
Bromobenzoate	9.4	2.0	39.8	8.7	42.9
Hydroxylbenzoate	46.4	3.5	0	<2	<1
Methoxybenzoate	48.9	10.6	24.8	12.6	21.3
Aminobenzoate	76.6	30.4	17.8	29.1	25.1
Dimethylaminobenzoate	25.5	0	0	0	0
Monomethyl benzenedicarboxylate	40.1	17.5	16.4	15.2	17.4
Nitrobenzoate	30.2	11.9	16.0	3.8	17.2

Table 3
Dipole moments and partial charges on selected electronegative atoms

Isomers	Dipole moment	O1*	O2*	X1*	X2*
2-Fluorobenzoate	9.69	−0.54	−0.57	−0.10	
3-Fluorobenzoate	9.89	−0.56	−0.56	−0.14	
4-Fluorobenzoate	9.96	−0.56	−0.56	−0.14	
2-Chlorobenzoate	9.56	−0.55	−0.55	−0.04	
3-Chlorobenzoate	11.28	−0.56	−0.56	−0.08	
4-Chlorobenzoate	11.97	−0.56	−0.56	−0.09	
2-Bromobenzoate	10.04	−0.55	−0.55	0.02	
3-Bromobenzoate	14.01	−0.56	−0.56	−0.02	
4-Bromobenzoate	15.60	−0.56	−0.56	−0.03	
2-Hydroxylbenzoate	8.16	−0.59	−0.55	−0.31	
3-Hydroxylbenzoate	9.40	−0.57	−0.56	−0.28	
4-Hydroxylbenzoate	10.83	−0.57	−0.57	−0.28	
2-Methoxybenzoate	7.52	−0.54	−0.58	−0.14	
3-Methoxybenzoate	10.59	−0.57	−0.56	−0.23	
4-Methoxybenzoate	13.05	−0.57	−0.57	−0.23	
2-Aminobenzoate	8.69	−0.59	−0.56	−0.33	
3-Aminobenzoate	11.41	−0.57	−0.57	−0.31	
4-Aminobenzoate	11.60	−0.57	−0.57	−0.31	
2-Dimethylaminobenzoate	7.66	−0.56	−0.56	−0.26	
3-Dimethylaminobenzoate	12.45	−0.57	−0.57	−0.24	
4-Dimethylaminobenzoate	14.64	−0.57	−0.57	−0.24	
2-Monomethyl benzenedicarboxylate	8.26	−0.57	−0.51	−0.44	−0.16
3-Monomethyl benzenedicarboxylate	11.69	−0.56	−0.56	−0.37	−0.29
4-Monomethyl benzenedicarboxylate	14.24	−0.56	−0.56	−0.39	−0.28
2-Nitrobenzoate	10.49	−0.53	−0.54	−0.40	−0.34
3-Nitrobenzoate	9.58	−0.54	−0.56	−0.38	−0.41
4-Nitrobenzoate	8.64	−0.55	−0.55	−0.40	−0.40

*O1 and O2 are the carboxylate oxygen atoms, X1 is the substituted electronegative atoms, such as F, Cl, Br, O; in the cases of nitrobenzoate and monomethyl benzenedicarboxylates, X1 and X2 are the two oxygen atoms on the nitro group or the carboxylate connected with methyl group.

3. Results and discussion

3.1. Characterisations

All the substituted benzoic acids, existing in three geometric isomeric forms and being referred hereafter as 2-, 3- and 4-isomers according to the position of the substituent to the carboxyl group (Fig. 1), were successfully intercalated in between the $[LiAl_2(OH)_6]$ layers by the ion-exchange reactions of $[LiAl_2(OH)_6]Cl \cdot H_2O$ with their potassium salts in 50% $H_2O/EtOH$ at 80 °C. The intercalates yielded were all the first stage intercalation compounds, $[LiAl_2(OH)_6]G \cdot xH_2O$ (x ca. 1–3.5; $G = XC_6H_4CO_2^-$, where $X = F$, Cl, Br, OH, OCH_3, NO_2, CO_2CH_3, NH_2, $N(CH_3)_2$). Invariably $Al(OH)_3$ was also formed in these reactions (Table 1), could be observed in several of the XRD patterns (Fig. 2).
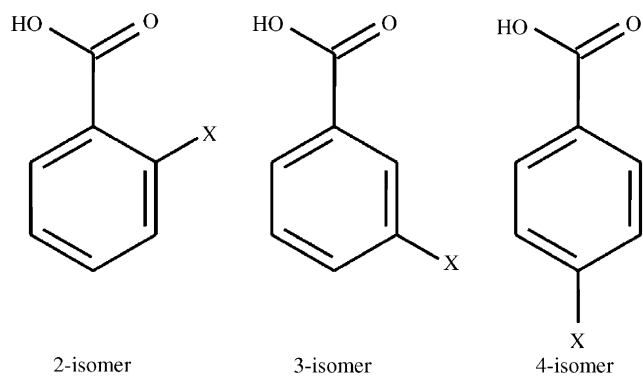
Fig. 1. Substituted benzoic acids, where X = F, Cl, Br, OH, OCH$_3$, NO$_2$, CO$_2$CH$_3$, NH$_2$, N(CH$_3$)$_2$.
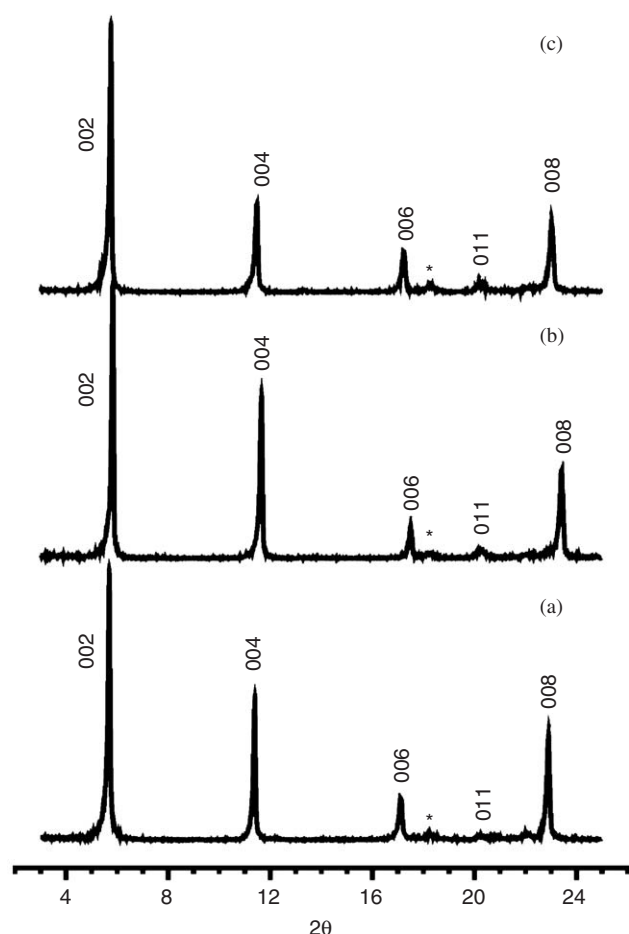

Fig. 2. XRD patterns of intercalation compounds of (a) 2-fluorobenzoate; (b) 3-fluorobenzoate and (c) 4-fluorobenzoate in Li/Al LDH. Peaks labelled with * belong to the Al(OH)$_3$ impurity.

The Al(OH)$_3$ comes from leaching of lithium ions during the intercalation, and some of it should be amorphous. In fact if [LiAl$_2$(OH)$_6$]Cl·H$_2$O is stirred with water it will deintercalate LiCl forming Al(OH)$_3$. We have studied this in some details using in situ powder diffraction [27]. Interestingly, it was found that 4-isomers always produced

smallest amount of Al(OH)$_3$ impurity and 2-isomers the most, as shown in both Table 1 and Fig. 2.

All the XRD patterns of the intercalation compounds are found to have at least three strong and almost equally spaced Bragg reflections at low angles in the angular dispersive XRD patterns (Fig. 2). Due to lack of data, the XRD patterns were only roughly checked and indexed with the program checkcell in Crysfire Package on a hexagonal cell [28]. The reflections were used to estimate the d spacings listed in Table 1.

The d spacings of the intercalates (Table 1) are found between 14.3 Å for [LiAl$_2$(OH)$_6$](4-nitrobenzoate)·2H$_2$O to 20.6 Å for one of the two phases of 3-dimethylamino-benzoate. These values are generally greater than one time of, but less than two times of, the length of the anions (distance between the centres of the carboxyl oxygen and of an atom on the other end, about 6–11 Å, according to the Cambridge Structural Database) plus a value of 7 Å (sum of the thickness of the hydroxide layer and all the related van der Waals radii), which probably means that the aromatic stacking effect is acting in these systems. The d spacings are also consistent with observations in literatures, and also as expected by a double layer structure [13,20,21]. As we know 4-nitrobenzoate is structurally similar to terephthalate and 2,5-PDA, it is not surprising that their intercalation compounds have similar d spacings (14.3 Å for 4-nitrobenzoate, 14.2 Å for terephthalate [21] and 14.0 Å for 2,5-PDA [20]).

Although most of the substituted benzoates can easily be intercalated by mixing the solution of the potassium salt with the LDH, it was found that a few derivatives were difficult to intercalate. For example, the first stage intercalation compound of 2-hydroxybenzoate, 3-hydroxybenzoate, 3-dimethylaminobenzoate and 3-nitrobenoate ware prepared using at high guest:host molar ratios (e.g. anion:LDH = 6:1).

3.2. Preferential intercalation studies

Since all the geometric isomers of these substituted benzoates can be intercalated into [LiAl$_2$(OH)$_6$]Cl·H$_2$O we were interested in determining if the host demonstrated a systematic anion preference. The competitive reactions were performed by the reactions of both equimolar binary and ternary isomeric mixtures with the host at 80 °C.

The percentage of each isomer intercalated into [LiAl$_2$(OH)$_6$]Cl·H$_2$O during these competition reactions were determined by solution ^{1}H NMR as reported previously [13,18,20,21] and are summarised in Table 2. Analysis of these results has allowed us to construct a general preference series (except aminobenzoate isomers):

$$4-\text{isomer} > 3-\text{isomer} > 2-\text{isomers}$$

Taking the bromobenzoate isomers as examples, Table 2 shows that 9.4% of the whole intercalated isomers is 2-bromobenzoate if an equimolar mixture of the 2- and 3-isomer is used for the intercalation; whilst only 2.0% is

2-bromobenzoate if it is mixed with the 4-isomer. These two results show that 3-bromobenzoate is more preferred by the LDH than 2-bromobenzoate, and that 4-bromobenzoate is the most preferred. This conclusion is consistent with the other results: in the case of binary equimolar mixture of 3- and 4-bromobenzoate, 39.8% of the whole intercalated isomers was 3-bromobenzoate; whilst in the case of ternary equimolar mixture, 8.7%, 42.9% and 48.4% were 2-, 3-, and 4-bromobenzoate, respectively.

We are most interested in determining what the critical factors are that control preferences to the anion by an LDH. As in the previous studies [13,18,20,21], we consider the observed phases are the thermodynamically favoured products under the conditions of the reaction. It is generally expected that the principal energy consideration is the electrostatic interaction between the positively charged metal hydroxide layer and the anions, and hydrogen bonds between the carboxyl oxygen atoms in the guest anions and hydroxyl hydrogen atoms in the hydroxide layers. As all of the guest anions have the same charge, same size and only one carboxylate group, we believe that the distribution of charges (dipole moment should be a good index for that in total) in the anions should play an important role.

In order to help us address some of these issues affecting the observed selectivities we have performed a series of theoretical calculation using the MOPAC in the CACHe package. We were able to compute the dipole moment for each anion by using AM1 at the minimum energy geometry. The minimum energy geometry was obtained by first optimising with augmented MM2 and then with MOPAC using AM1 parameters. AM1 dipole moments have an average difference between experimental and observed values of 0.35 Debye [26]. A summary of selected results of these calculations is given in Table 3, which shows that in the most cases, the dipole moment series are (except for the nitrobenzoate anions, which have reversed sequences and can be understood if we notice that $-NO_2$ is an electron withdrawing group):

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

Compared with the series abstracted from competitive intercalation reactions, the above series is generally the same although there are two exceptions (nitrobenzoate isomers in the dipole moment series and aminobenzoate isomers in the competition series). This is in accordance with the considerations from viewpoint of both static interactions and H-bonding, as we know from the calculations that the charges on oxygen atoms of carboxyl group are around -0.55, which means H-bonding is about the same, and therefore static interactions is the main issue that cause differences.

The halogenated benzoate experiments supply evidence on the factor of dipole moment. Fig. 3 shows a plot of the percentages of less preferred component in the binary intercalates versus the difference of their dipole moments.
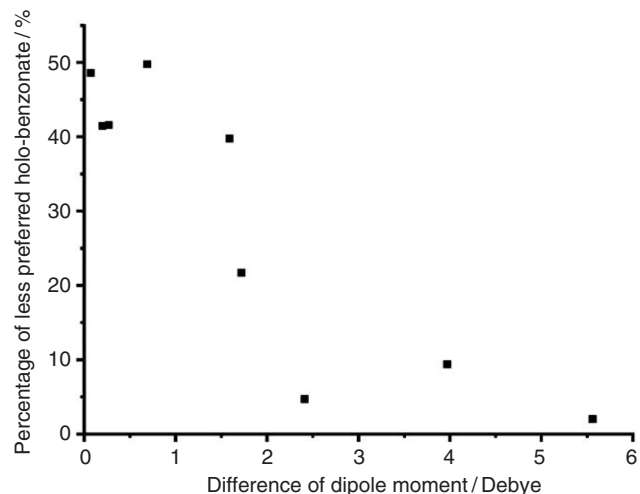

Fig. 3. The relationship of the percentage of less preferred halogenated benzoate isomer and the difference of dipole moments of the isomers in binary mixture.

It can be seen that as the difference of dipole moments increases, the selectivity generally increases.

Undoubtedly, the factors that determine the preferences are much more complicated [2,13,14,17,18,20,21]. This is especially true when the substituted groups become complicated and able to form hydrogen bonds with hydroxyl groups in the layers. In the present case, we believe that electronegative atoms at the ortho-position of carboxylate group should be more important because they are able to interact with the layer hydroxyl hydrogen atoms. If we take this interaction into account, we may explain why 2-isomers can gain such large percentages (30–77%, Table 2) in the competitions of 2-isomers and 3-isomers when compounds such as hydroxylbenzoate, methoxylbenzoate, aminobenzoate, monomethylbenzenedicarboxylate and nitrobenzoate are used: all those compounds contain nitrogen and oxygen atoms that are available for hydrogen bonding.

4. Conclusions

All the geometric isomers of a series of substituted benzoates were intercalated successfully into the LDH, $[LiAl_2(OH)_6]Cl \cdot H_2O$ at 80 °C. In all cases the 4-isomers always produced the purest intercalation compounds, while the 2-isomers produce the most impure compounds with the largest amount of $Al(OH)_3$.

The LDH host shows remarkable intercalation preference for these isomer anions in ethanol/water solution, if there is a large difference in dipole moment. The host selects anions based on their ability to interact with the positively charged layers if other conditions remain the same. Among all the interactions, the interaction between carboxylate oxygen atoms and the layers, which includes both hydrogen bonding and static interaction, is of the first importance; the interaction between dipole moments and layers is of secondary importance. Furthermore,

other interactions such as hydrogen bonding from non-carboxyl-oxygen atoms, and also interactions among anions (e.g. aromatic stacking effect) should be considered.

Acknowledgments

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