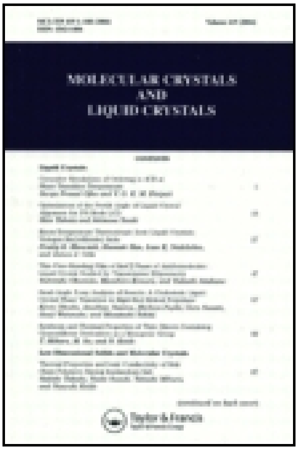

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New Regioselective Intercalation Reactions

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New Regioselective Intercalation Reactions

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The ordered layered double hydroxide, $[LiAl_2(OH)_6]Cl.2H_2O$ exhibits shape-selective ion-exchange intercalation of dicarboxylate anions. Specific isomeric preferences can be controlled by varying the reaction temperatures. The intercalated guests can be quantitatively recovered from the host lattice with concomitant regeneration of the host offering a novel approach in separation science. To illustrate the potential of this new material in separation science, we describe the isolation of pure 1,4-benzenedicarboxylate and 2,6-naphthalenedicarboxylate from mixtures of their isomers. The neutral organic acids are both monomers in the synthesis of a range of important polyesters.

Keywords: Intercalation; Shape-Selectivity; Kinetics; X-Ray Diffraction

INTRODUCTION

The design of solids that can selectively and reversibly bind molecules, i.e. "*molecular recognition*", has been the subject of much recent interest. [1] Such specific associations are ubiquitous in biology but they also lie at the heart of important practical chemical technologies such as chemical sensing [2,3,4], separations [5], and catalysis [6]. The design of lamellar inorganic hosts such as clays, phosphates, phosphonates and modified thin films that exhibit molecular recognition features have recently been reviewed by Mallouk and Gavin [7].

In lamellar inorganic solids, guest molecules access intracrystalline binding sites via intercalation reactions. Normally, intercalation is driven by relatively unselective processes including oxidation-reduction, ion-exchange, or acid-base reactions. The interlamellar gallery expands to accommodate the guest species resulting in little size- or shape-selectivity to the reaction.

RESULTS AND DISCUSSION

Layered double hydroxides (LDH) have been the focus of much research as a result of their potential applications in fields as diverse as catalysis, medicine and ion scavenging. We and others have recently shown that there is ordering of the cations in the layers of the layered double hydroxide $[LiAl_2(OH)_6]_2CO_3.nH_2O$ with the Li^+ ions located in the vacant octahedral holes of a Gibbsite-like array of Al^{3+} cations [9,10]. More recently we have refined the structures of the dehydrated intercalation compounds $[LiAl_2(OH)_6]X$ (X = Cl, Br, NO_3) and the hydrated analogue $[LiAl_2(OH)_6]Cl.H_2O$ using the same layer model [10]. In the dehydrated compounds the guest anions occupy trigonal prismatic sites between Li^+ cations in adjacent layers.

Here we describe the separation of aromatic dicarboxylates from isomeric mixtures using shape-selective intercalation in $[LiAl_2(OH)_6]Cl.H_2O$.

Separation of Benzenedicarboxylates

Reaction of the double layer hydroxide $[LiAl_2(OH)_6]Cl.H_2O$ with different isomers of the disodium salts of 1,2-, 1,3- or 1,4-benzenedicarboxlyate anions (ie. phthalate, isophthalate, terephthalate anions respectively) in H_2O yields the 1st stage intercalation compounds $[LiAl_2(OH)_6]_2[G].xH_2O$ ($x = 4$, or 5; G = 1,2-$C_8H_4O_4$, 1,3-$C_8H_4O_4$, 1,4-$C_8H_4O_4$) respectively [11]. However, when an equimolar solution of all three disodium salts is added to $[LiAl_2(OH)_6]Cl.H_2O$ only $[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4].4H_2O$ is isolated from the reaction [11]. The X-ray diffractogram of this material is identical to a sample prepared by direct reaction of $[LiAl_2(OH)_6]Cl.H_2O$ with $(Na^+)_2(1,4\text{-}C_8H_4O_4^{2-})$.

We have investigated the selective intercalation of these benzenedicarboxylate anions in $[LiAl_2(OH)_6]Cl.H_2O$ using time-resolved, in-situ energy dispersive X-ray diffraction. These experiments confirmed that these reactions are remarkably facile with a typical half life ($t_{1/2}$) of *ca.* 1-2 minutes at room temperature. At the very early stages following addition of the guests a new crystalline kinetic phase was detected with a d-spacing of 15.1Å. The interlayer spacing of this crystalline phase does not correspond to any of the pure benzenedicarboxylate intercalate phases. Subsequently, this phase decays giving the 1,4-benzenedicarboxylate intercalate with a d-spacing of 14.3 Å. We believe that the crystalline intermediate phase can be attributed to a LDH intercalate containing all three organic acids and that under the conditions of the reaction the thermodynamically most stable phase is the one in which only terephthalate anions remain within the layers.

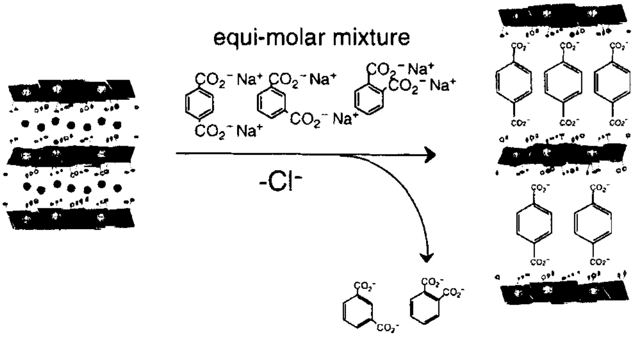

FIGURE 1 Preferential intercalation of terephthalate in $[LiAl_2(OH)_6]Cl.H_2O$ at room temperature in water. The isolated intercalate phase contains 95% terephthalate and 5% phthalate anions.

We are able to ion-exchange the intercalated ions out of this material by stirring with Na_2CO_3 in water overnight. The solution ^1H NMR spectrum of the supernatant solution following ion-exchange with Na_2CO_3 was dominated by the resonances due to $(Na^+)_2(1,4\text{-}C_8H_4O_4^{2-})$ together with a small amount of $(Na^+)_2(1,2\text{-}C_8H_4O_4^{2-})$. The integration of the ^1H resonances due to each isomer allows us to quantitatively determine the isomeric preferences. The degree of selectivity for intercalation of the terephthalate in $[LiAl_2(OH)_6]Cl.H_2O$ was estimated to be in excess of 95% (Figure 1).

Separation of Naphthalenedicarboxylates

We have also investigated the intercalation preferences of the 1,5- and 2,6-naphthalenedicarboxylates in $[LiAl_2(OH)_6]Cl.H_2O$. Addition of an equimolar mixture of $Na^+_2\{1,5\text{-}C_{10}H_6(CO_2^-)_2\}$ and $Na^+_2\{2,6\text{-}C_{10}H_6(CO_2^-)_2\}$ to a suspension of $[LiAl_2(OH)_6]Cl.H_2O$ in water at 100 °C results in the isolation of a single 1st stage intercalation compound with an interlayer separation of 16.6Å. The X-ray powder pattern of this material is identical to that exhibited by the product of the direct intercalation of $2,6\text{-}C_{10}H_6(CO_2^-)_2$ in $[LiAl_2(OH)_6]Cl.H_2O$. Treatment of the isolated solid with Na_2CO_3 in D_2O allows us to quantify the specific preferences by solution NMR. The integration of the ^1H resonances of the guest ions exchanged out of the solid indicate that over 99% of the intercalated ions were $Na^+_2\{2,6\text{-}C_{10}H_6(CO_2{}^-{}_2\}$.

CONCLUSIONS

The ability of $[LiAl_2(OH)_6]Cl.H_2O$ to preferentially intercalate specific organic carboxylic acids could have significant impact in the field of separation science. The purification of terephthalic acid is a major industrial business as it is used as a monomer in a range of polyesters. In addition, the widespread use of 2,6-napthalenedicarboxylic acid in the synthesis of new higher performance polyesters is currently limited partly due to the cost of purification of the acid feedstock.

We have carried out some preliminary experiments which show that $[LiAl_2(OH)_6]OH.H_2O$ can also be used to separate these acids. The acids can be selectively intercalated into the host. The solid intercalate can then be collected by filtration, washed with water and treated with Na_2CO_3 to generate $[LiAl_2(OH)_6]_2CO_3.H_2O$ and $Na^+_2\{2,6\text{-}C_{10}H_6(CO_2^-)_2\}$. Finally, the regeneration of the ion-exchange capacity of the LDH is accomplished by a initial calcination and then mild hydrothermal treatment. Further large scale studies are in progress, as are investigations into the long term stability of the host structure following multiple regeneration cycles.

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