Staging of Organic and Inorganic Anions in Layered Double Hydroxides

**J. Pisson,‡ C. Taviot-Guého,*,§ Y. Israëli,‡ F. Leroux,§ P. Munsch,† J.-P. Itié,† V. Briois,†
N. Morel-Desrosiers,‡ and J.-P. Besse§**

*Laboratoire des Matériaux Inorganiques, UMR 6002, Université Blaise Pascal (Clermont-Ferrand II),
24 avenue des Landais, 63177 Aubière Cedex, France, and Laboratoire pour l'Utilisation du Rayonnement
Electromagnétique, Bât 209D, Centre Universitaire Paris Sud, BP 34, 91898 Orsay Cedex, France, and
Laboratoire de Thermodynamique des Solutions et des Polymères, UMR 6003, Université Blaise Pascal
(Clermont-Ferrand II), 24 avenue des Landais, 63177 Aubière Cedex, France*

The layered double hydroxides (LDHs) $Zn_2Al(OH)_6Cl \cdot nH_2O$, $Zn_2Cr(OH)_6Cl \cdot nH_2O$, and $Cu_2Cr(OH)_6Cl \cdot nH_2O$ have been shown to undergo staged intercalation reactions with succinate and tartrate anions. Monitoring the process in situ using energy-dispersive X-ray diffraction reveals the formation of second-stage intermediates caused by the filling of every second layer. Depending on the nature of the organic anion, the Bragg peaks of the second-stage intermediates and the fully organic exchanged materials emerge in two distinct sequences indicating two exchange pathways. For tartrate exchange, the fully exchanged material is not observed until the intermediate has gone through its maximum and the chloride precursor has disappeared completely, while for succinate exchange, the final state of intercalation and the second-stage intermediate simultaneously appear. Similar staging has previously been reported only for $LiAl_2(OH)_6Cl \cdot 2H_2O$. These results demonstrate that staging in the intercalation of LDH does not involve a structural order of the host and cannot be explained by a tactoid mechanism.

Introduction

The exchange capacity of layered double hydroxides (LDHs), described by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{m-}_{x/m} \cdot nH_2O]$, allows for the preparation of a wide range of host−guest complexes. Of particular interest are the organic−inorganic hybrid LDHs owing to their very large field of application as catalysts, electrochemical sensors, or sorbents for organic pollutants.[1] Besides, recent developments on 2D nanocomposite materials have been reported that describe the nanoscale assembly of organic polymers and LDHs, enlarging these applications for those emphasizing mechanical enhancement.[2]

Most of the articles concerned with inorganic/organic anion-exchanged LDH generally describe the fully exchanged materials, and surprisingly, few investigations have been reported on mixed organic−inorganic ion-exchanged forms obtained at partially exchanged rates. The reason may be that phase segregation is generally admitted for the exchange process in LDH, in which a mixture of starting material and newly formed LDH is obtained. However, the frequent contamination of LDH by carbonate species from air can be viewed as a co-intercalation phenomenon leading to a mixed ion structure in which the interlayer is occupied by both anions. Mixing of two ions at exchange sites can also lead to a phenomenon of interstratification with the random or ordered stacking of two types of interlayers. The regular stacking is referred to as staging, which is commonly observed in the graphite system. The first

description of a staging mechanism proposed by Rudorff involves the filling of every *n*th layer in the *n*th stage compound.[3] Yet, owing to the scarcity of staging phenomena in lamellar materials other than graphite, it then has been interpreted in terms of the stiffness of host planes.[4,5] It is believed that staging occurs via a domain model, first proposed by Daumas and Hérold,[6] resulting from guest species diffusion toward the crystal center and only possible if the host layers are flexible, as are the single-carbon honeycomb sheets of graphite.

Recently, in situ time-resolved X-ray diffraction studies on intercalation compounds have been reported by O'Hare et al.[7] These authors have shown the interest of this technique in solid-state kinetics and, particularly, in the intercalation chemistry of lamellar materials. In this way, they have demonstrated the ability of $[LiAl_2(OH)_6Cl \cdot 2H_2O]$ to form second-stage intermediates, that is, filling of every second layer during the intercalation of dicarboxylate anions (succinate, tartrate, adipate, fumarate, maleate, L-malate, phthalate, terephthalate).[8a] Staging in such materials should not be observed according to the theoretical models given the rigidity of the layers (five atoms thickness). Though not clearly specified by the authors, one might think, in a first place, that staging in $[LiAl_2(OH)_6Cl \cdot 2H_2O]$ LDH, which is a rare example of LDH presenting an ordered arrangement of metal cations, stems from this structural singularity.[8b,c] However, quite recently, phenomena related to staging have also been reported for [Mg−Al]-based layer double hydroxides by direct synthesis of mixed hydroxide/azobenzene (AzAA) intercalates[9] and during the exchange of interlayer terephthalate anions by chloride and nitrate anions.[10] From these few reported cases, it appears that staging can happen either throughout the exchange process or by direct synthesis and is associated with different interlayer contents or different orienta-

* To whom correspondence should be addressed. E-mail: gueho@chimsrv1.univ-bpclermont.fr.

‡ Laboratoire de Thermodynamique des Solutions et des Polymères, UMR 6003, Université Blaise Pascal (Clermont-Ferrand II).

§ Laboratoire des Matériaux Inorganiques, UMR 6002, Université Blaise Pascal (Clermont-Ferrand II).

† Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bât 209D, Centre Universitaire Paris Sud.

tions of the same molecule. The conditions for the appearance of staging in a LDH system are thus various, but the reasons it takes place have not been clearly established yet. For Kaneyoshi et al., the interstratification is originated from two orientations of terephthalate anions within the layers, vertical and horizontal, which can be controlled by varying the layer charge density and the extent of drying.[10] On the other hand, Iyi et al.,[9] for the direct synthesis of mixed hydroxide/azobenzene (AzAA) intercalates, assume a segregation of the hydrophobic organic anions and the hydrophilic inorganic anions, similar to that reported for staged fluorohectorite clays;[11] bipolar nanoparticles or "tactoïds" are thus formed in solution that subsequently transform into staging structures when dried.

Besides the structural interest, such staging-like behaviors of LDHs are of major importance for future developments in the intercalation chemistry of these compounds. New hybrid materials could thus be prepared, combining the physicochemical properties of two ion-exchanged forms.

To get further insights on the staging behavior of LDH, we have investigated the exchange process of a series of LDHs: $Zn_2Al(OH)_6Cl \cdot nH_2O$, $Zn_2Cr(OH)_6Cl \cdot nH_2O$ and $Cu_2Cr(OH)_6Cl \cdot nH_2O$, abbreviated hereafter as [Zn_2Al-Cl], [Zn_2Cr-Cl], and [Cu_2Cr-Cl], respectively. In the present work, we were particularly interested to determine whether staging could be related to the chemical composition of the hydroxide layers or the interlayer species. By the chemical composition of the hydroxide layers, we also refer to the cationic ordering. Indeed, while there is no evidence for cationic order in the brucite-like layers of [Zn_2Al-Cl], local description of the arrangement around cations by extended X-ray absorption fine structure (EXAFS) at K edge concluded unambiguously for [Zn_2Cr-Cl] and [Cu_2Cr-Cl] to a cationic ordering.[12] By this technique, a corrugation of [Cu_2Cr-Cl] hydroxide layers was also shown because of the Jahn–Teller distortion in Cu^{2+} octahedra, whereas [Zn_2Al-Cl] and [Zn_2Cr-Cl] sheets present a relative flatness. Using in situ energy-dispersive X-ray diffraction, we followed the exchange of chloride anions in [Zn_2Al-Cl], [Zn_2Cr-Cl], and [Cu_2Cr-Cl] by two carboxylate anions A^{2-}, tartrate ($^-O_2C(CHOH)_2CO_2^-$) and succinate ($^-O_2C(CH_2)_2CO_2^-$). The anion exchange of ZnAl and ZnCr LDH phases with tartrate and succinate anions has already been reported, and a lower degree of exchange for tartrate was mentioned ascribed to the OH functions.[13,14] Therefore, in the second place, by comparing the exchange process of tartrate and succinate anions, we aim to further investigate the effect of the OH groups and hydrogen bonds in the host/guest interactions.

Experimental Section

Synthesis. The starting chloride LDHs were prepared by direct coprecipitation[15] at room temperature and under nitrogen atmosphere. Typically, a 40 mL portion of an aqueous solution containing a mixture of divalent metal chloride (0.66 M) and trivalent metal chloride (0.33 M) was added at a rate of 0.16 mL/min in a flask containing 150 mL of deionized and decarbonated water under vigorous stirring. A solution of sodium hydroxide (2 M) was simultaneously added. This addition was monitored by a pH regulator via a pH electrode immersed in the reagent solution to fix the pH of coprecipitation at 8.0 for the preparation of [Zn_2Al-Cl], 5.5 for that of [Zn_2Cr-Cl], and 4.9 for that of [Cu_2Cr-Cl]. Once the addition was complete, the resulting precipitates were aged for 24 h in the mother liquid. The LDH materials were recovered by three dispersion and centrifugation cycles in water and were finally air-dried.

Elemental analyses were performed in the Vernaison Analysis Center of CNRS by inductively coupled plasma (ICP) emission
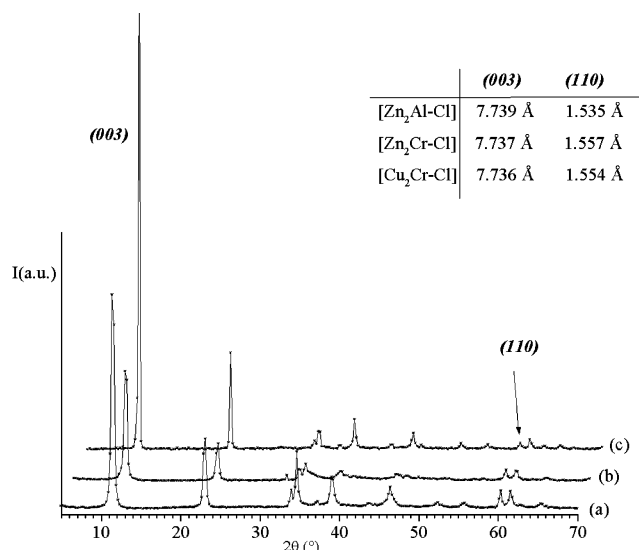

Figure 1. PXRD patterns of (a) [Zn_2Al-Cl], (b) [Zn_2Cr-Cl], and (c) [Cu_2Cr-Cl] prepared by coprecipitation.

TABLE 1: Chemical Composition of Precursor Compounds

LDH	M^{2+}/M^{3+}	Cl^-/M^{3+}	H_2O/M^{3+}
[Zn_2Al-Cl]	1.94	0.90	1.52
[Zn_2Cr-Cl]	1.98	1.00	1.90
[Cu_2Cr-Cl]	2.2	1.10	1.90

spectroscopy. The chemical analysis of these chloride precursors given in Table 1 confirms a typical composition of anionic clays with a M^{2+}/M^{3+} molar ratio close to 2. The powder X-ray diffraction patterns presented in Figure 1 also indicate the formation of pure LDH compounds of relatively good crystallinity.

For the preparation of tartrate fully exchanged material [Zn_2-Cr-tartrate] and the second-stage intermediate [Zn_2Cr-$Cl/$ tartrate], conditions similar to those for the energy-dispersive X-ray diffraction (EDXRD) experiments were used. [Zn_2Cr-tartrate] was obtained by stirring overnight about 1.5 g of the chloride precursor dispersed in a solution of sodium tartrate containing an excess of 2.5 equiv of tartrate anions over the Cr^{3+} content. For the synthesis of the second-stage intermediate, the amount of tartrate anions used corresponds to the anionic exchange capacity (AEC), that is, $A^{2-}/Al^{3+} = 0.5$. All of the procedures were performed with deionized and decarbonated water under nitrogen atmosphere.

Physical Measurements. Powder X-ray diffraction patterns (PXRD) were recorded on a X'Pert Pro Philips diffractometer using Cu Kα radiation. The vacuum-drying experiments were carried out with a HTK16 Anton Paar chamber and a PSD-50m Braun detector.

Energy-dispersive X-ray diffraction (EDXRD) experiments were performed at the LURE synchrotron facility (Orsay, France) using X-ray synchrotron radiation emitted by the DCI storage ring (1.85 GeV positrons, average intensity of 250 mA) at the DW 11 beam line. The white beam was collimated down to 200 (vertical) by 80 (horizontal) μm^2 with a system of two successive slits. The diffracted spectra were collected with a Ge detector set at a fixed diffraction angle ($2\theta = 5.94°$). Depending on the chosen angle, a large range of d-spacings can be observed between 10 and 60 keV (typically a range from 11 to 2 Å). The slits, which define the diffraction angle, act as Soller slits and therefore reduce the diffraction from the background.

The reaction cell was a thermostated Teflon cell[16] possessing two Kapton windows and an optical path length of 6 mm. It
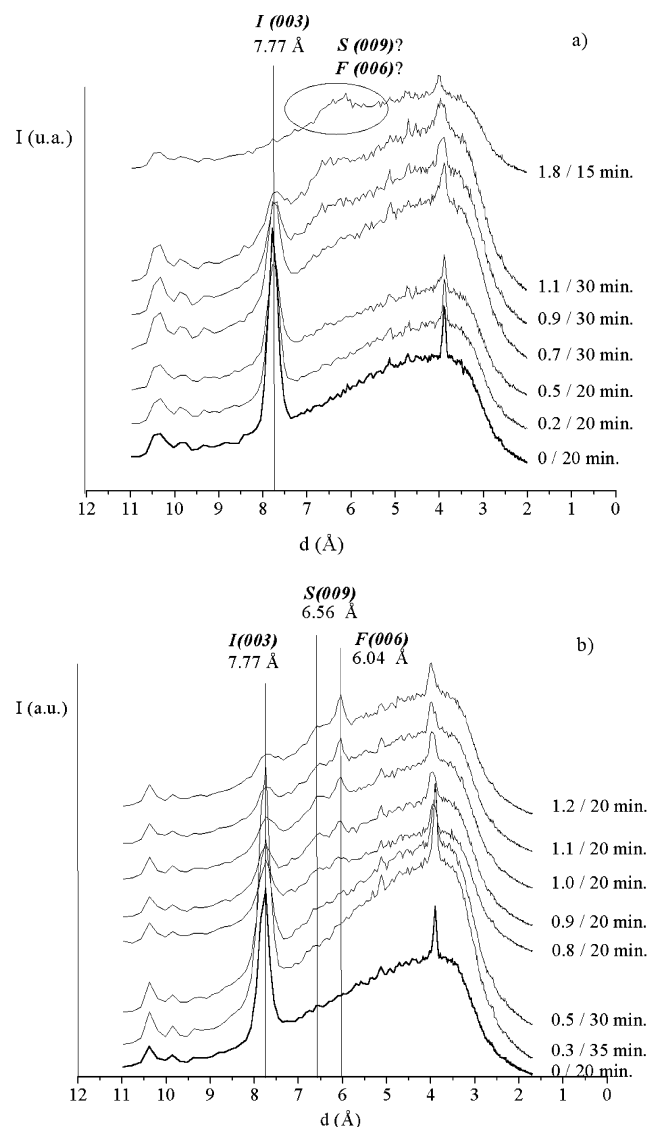
Staging of Organic and Inorganic Anions

J. Phys. Chem. B, Vol. 107, No. 35, 2003 **9245**

Figure 2. In situ energy-dispersive X-ray powder diffraction data showing the course of the anion-exchange reaction (a) between [Zn$_2$-Al−Cl] and tartrate anions and (b) between [Zn$_2$Al−Cl] and succinate anions. The patterns are displaced vertically with added organic content from bottom to top. The A^{2-}/LDH starting ratios in solution converted into theoretical exchange rates and the acquisition time are given on the right in front of each spectra. I denotes chloride precursor, S denotes second-stage intermediate, and F denotes fully exchanged material.

was filled with an aqueous suspension of chloride precursors (about 100 mg of LDH dispersed in 3 mL of deionized and decarbonated water) constantly stirred to prevent the solid from settling. Aqueous solutions of the carboxylate anions (0.214 M) were added dropwise to the cell from a syringe pump. Individual spectra were collected at different A^{2-} to LDH starting ratios in solution, from which theoretical exchange rates were calculated. Acquisition times ranged from 5 to 30 min depending on the reaction rate. The large background hump is due to scattering from the organic aqueous solutions convoluted with the spectral curve of the incident beam.

Results and Discussion

Evidence of Staging Phenomenona. Energy-dispersive XRD patterns from the in situ exchange reactions are presented Figures 2−4, and d_{hkl} distances are reported Table 2. They were recorded at different starting A^{2-}/LDH ratios in solution converted into theoretical exchange rates, as already mentioned.
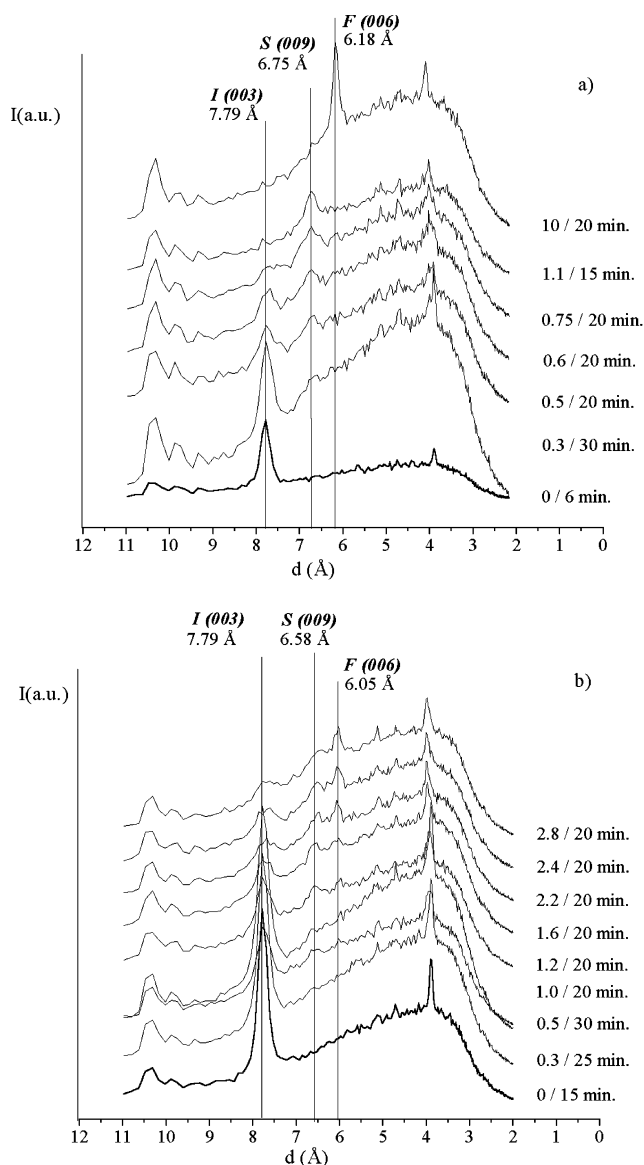

Figure 3. In situ energy-dispersive X-ray powder diffraction data showing the course of the anion-exchange reaction (a) between [Zn$_2$-Cr−Cl] and tartrate anions and (b) between [Zn$_2$Cr−Cl] and succinate anions.

The spectra of the starting LDHs before organic additions were relatively similar among each other. The reflections were indexed in a hexagonal lattice with the $R\bar{3}m$ rhombohedral symmetry. All of these chloride precursors exhibit the same interlayer distance, close to 7.8 Å; the 006 reflection around 3.9 Å is also visible. The small peaks at 5.12 and 4.70 Å correspond to parasitic peaks of the setup, while the peaks at 10.4 and 9.8 Å are due to Zn fluorescence (Kα and Kβ, respectively). It is noteworthy that the interlayer distances of these water-suspended LDHs do not differ from those in the dried state. This may indicate that either the water molecules do not enter the interlamellar space or the interlamellar distances are not determined by the amount of water. This result is consistent with a previous study on the hydration state of LDHs in which no evolution of the basal spacing in relation to the humidity of the atmosphere was observed with monovalent anions and a M^{2+}/M^{3+} molar ratio equal to 2; the resulting high interlayer packing density limits the space available for intracrystalline water molecules.[17]

Two reaction products, called F and S phases, were identified during the intercalation process. Their Bragg reflections were
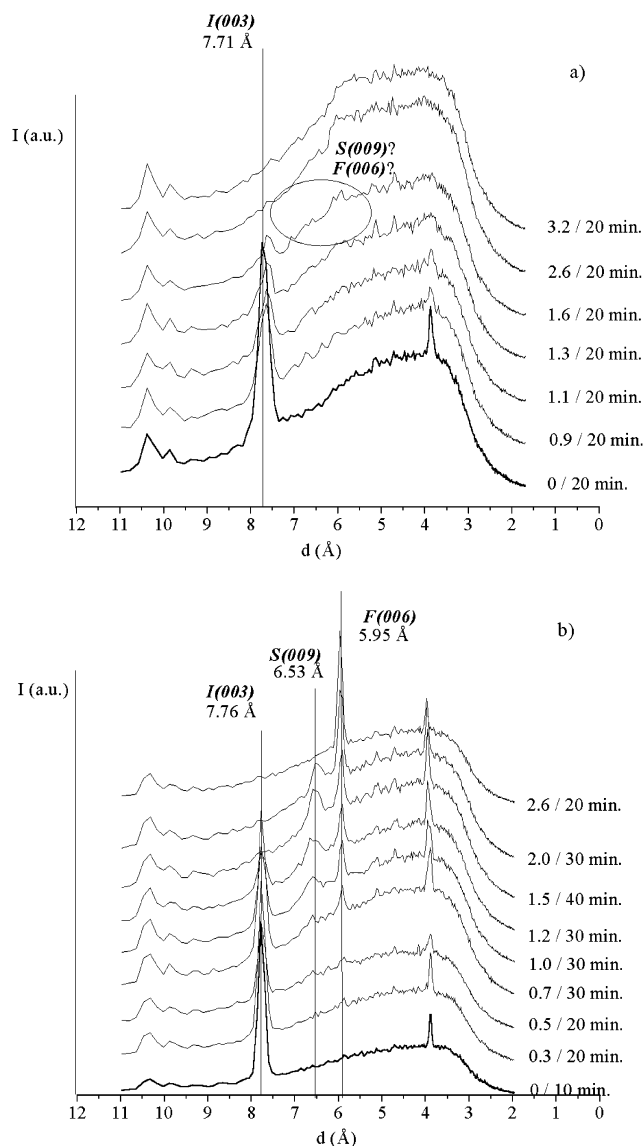
Figure 4. In situ energy-dispersive X-ray powder diffraction data showing the course of the anion-exchange reaction (a) between [Cu₂-Cr−Cl] and tartrate anions and (b) between [Cu₂Cr−Cl] and succinate anions.

TABLE 2: Summary of EDXRD Data for Intercalation Compounds[a]

	I(003) Å	S(009) Å		F(006) Å	
		tartrate	succinate	tartrate	succinate
[Zn₂Al−Cl]	7.77		6.56		6.04
[Zn₂Cr−Cl]	7.79	6.75	6.58	6.18	6.05
[Cu₂Cr−Cl]	7.71		6.53		5.95

[a] I denotes chloride precursor, S denotes second-stage intermediate, and F denotes fully exchanged material.

also indexed considering a hexagonal lattice with the $R\bar{3}m$ rhombohedral symmetry. F phase is the fully exchanged material with an interlayer spacing of 12.1 Å for succinate and 12.4 Å for tartrate ($2d_{006}$); similar values were obtained elsewhere for samples dried in air at room temperature and were attributed to A^{2-} anions vertically orientated to the layers.[14] The S phase is the second-stage intermediate with an interlayer spacing of approximately 19.7 Å for mixed succinate/chloride LDH and 20.2 Å for mixed tartrate/chloride LDH ($3d_{009}$). These values are equal to the sum of starting and the fully exchanged materials, indicating the regular interstratification of the two

unit layers. These *d* spacings were determined from the position of the 009 reflection of the second-stage intermediates for the experimental setup did not allow the 003 nor the 006 reflections to be observed. The 0015 reflection though visible was not considered either in the following discussion because it almost superimposes on both the 006 reflection of the chloride precursors and the 009 reflection of the fully exchange materials.

No other intermediate phases of higher-order staging were detected in the *d* spacing range from 11 to 2 Å, in any of these reactions. Neither was observed a variation of the *d* spacing of the present S phases that would be attributed to a variation of the number of the layers intercalated by A^{2-}, as reported for staged fluorohectorite clays.[11] We also exclude the formation of an interstratified phase associated with two orientations of the A^{2-} anions, vertical and horizontal to the layers, as reported for terephthalate anions.[10] The occurrence of a flat orientation for tartrate and succinate anions under ambient conditions has never been reported so far. Previous studies on the intercalation of alkanedioic acids and for different charge density of the host layers[18] have shown a linear increase of the interlamellar distance with the number of carbon atoms, which supports the vertical orientation.

The extent of the exchange reaction is first marked by the gradual decrease of the intensity of the (003) reflection of the chloride precursors as the A^{2-}/LDH ratio is increased. The appearance of the second-stage intermediate is more or less obvious depending on both the LDH matrix and the dicarboxylate anion. Yet, for [Zn₂Cr] host, the changes in the EDXRD patterns show clearly staging-like behaviors for the two anions (Figure 3). In this case, it is first remarkable that the growth of the (009) reflection of both S phases occurs exactly at the same theoretical exchange rate, that is, 0.3. For tartrate exchange, it looks as if the 006 reflection of the fully exchanged material (F) is not observed until the intermediate (S) has gone through its maximum and the chloride precursor (I) has disappeared completely. Conversely, for succinate exchange, the fully exchanged material is observed at the same time as the second-stage intermediate. [Zn₂Al] and [Cu₂Cr] hosts exhibit similar sequences of peaks (Figures 2 and 4), although the formation of the tartrate second-stage intermediates is less obvious leading to broad bands that cannot be easily assigned. This amorphization cannot be attributed to a lower crystallinity of the corresponding chloride precursors because the widths of the (003) reflections of [Zn₂Al−Cl] and [Cu₂Cr−Cl] are narrower than that of [Zn₂Cr−Cl] in the dried state. A possible explanation could be that the present exchange reactions were conducted without controlling the pH, which is well-known to highly influence the crystallinity of the products. Nevertheless, on the whole, the intercalation of tartrate anions appears more sluggish than that of succinate anions, or longer equilibration times are needed for tartrate exchange. Indeed, the fully exchanged succinate compounds are formed at the initial stages of the anion addition, whereas the fully tartrate exchanged materials, only visible in the case of [Zn₂Cr], appear at high A^{2-}/LDH ratio. Previous studies have already mentioned that tartrate anions do not exchange as easily as the other alkanedioate salts because of the complexing power of tartrate anions, which react spontaneously with metallic cations and oxides, impeding the intercalation.[14]

Interpretation and Comparison to Other Systems. These two distinct peak sequences in the EDXRD patterns led us to consider two exchange pathways, determined by the chemical properties of the organic anion. The fact that first and second staging for succinate anions appear simultaneously might

Staging of Organic and Inorganic Anions

J. Phys. Chem. B, Vol. 107, No. 35, 2003 **9247**

indicate that the actual reaction pathway involves an additional reaction of the fully exchanged materials with the chloride precursors. Such a transitional reaction has already been proposed for explaining the formation of staged fluorohectorite clays.[11] Succinate anions with van der Waals interactions between alkyl chains would compete effectively with chloride anions during the exchange process and some fully exchanged material, along with second-staged intermediate, is formed at initial stages of the addition, which then further reacts with the chloride precursor. Conversely, tartrate anions cannot quantitatively displace chloride anions from exchange sites because of the complexing power of the anion reported above, and high tartrate concentrations are needed to shift the equilibrium in favor of the second-staged intercalate, which then converts into the fully exchanged material.

Our results on succinate anions are quite different from those reported by O'Hare et al. on $LiAl_2(OH)_6Cl \cdot 2H_2O$,[8a] for which the fully exchanged material is not observed until the intermediate has gone through its maximum and the host has decayed completely. Similar behaviors with other dicarboxylate salts were obtained, but unfortunately, the study did not include the tartrate anions. Such an intercalation process resembles more the behavior that we observed with tartrate anions. However, comparing these different published results is not an easy task because the experimental conditions and setup were not rigorously the same.

Regarding the reasons staging occurs in the intercalation of LDH, our results demonstrate that staging does not involve a structural order of the host. Indeed, contrary to $LiAl_2(OH)_6Cl \cdot 2H_2O$, the present compounds exhibit a quasi-random or local cation distribution within the hydroxide layers.[18] It is also worth noting that the corrugation of $[Cu_2Cr]$ hydroxide layers does not prevent nor facilitate the staging.

On the other hand, staging here is not believed to arise from the formation of bipolar two-nanolayer tactoids as proposed by Ijdo et al.[11] in the mica system and Iyi et al.[9] for mixed hydroxide/azobenzene intercalates of Mg–Al LDH. They assume that because of the hydrophobic binding effect or the size effect of the organic anions compared to the layer charge density or both, the inorganic anions are excluded from the interlayer space of two-layer nanoclay particles leading to the formation of bipolar tactoids; staging structures are then formed upon stacking of the tactoids during the drying step. This tactoid hypothesis is not plausible here considering the exchange reaction used for synthesis and the large size of chloride precursor particles (ca. 1 μm). Besides, extended staged structures start forming in solution, in the present case. Yet, we do not exclude a segregation between hydrophobic organic anions and hydrophilic inorganic anions, which could be proposed as the pathway for staging behavior in the intercalation of LDH.

Structural Evolution of Tartrate Second-Stage Intermediate under Vacuum-Drying. To further characterize this staging phenomenon, the synthesis of $[Zn_2Cr]$ tartrate second-stage intermediate was attempted. While it was observed as a single phase in the EDXRD patterns after the addition of an amount of organic corresponding to 1.1 times the AEC, we were unsuccessful in isolating it in laboratory conditions; the fully exchanged material was always present, together with the second-stage intermediate. It is highly likely that discrepancy arises from the difference between the in situ EDXRD experiments for which the exchange procedure was fractionized in the time and the one-step anion-exchange procedure employed. The resulting XRD pattern is presented Figure 5 for a sample
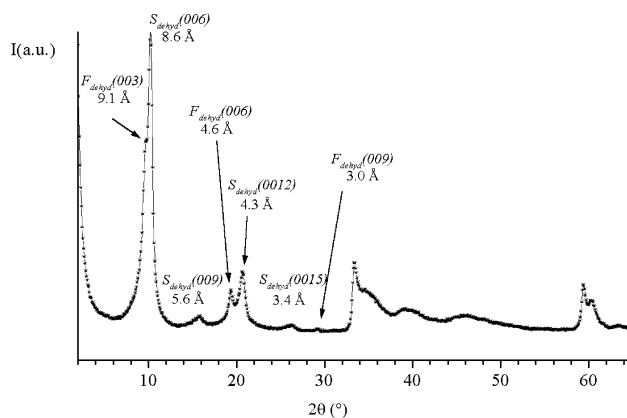

Figure 5. PXRD patterns of $[Zn_2Cr-Cl]$ exchanged with tartrate anions for $A^{2-}/Cr^{3+} = 0.5$. The measurement is for a sample dried at room temperature under vacuum.
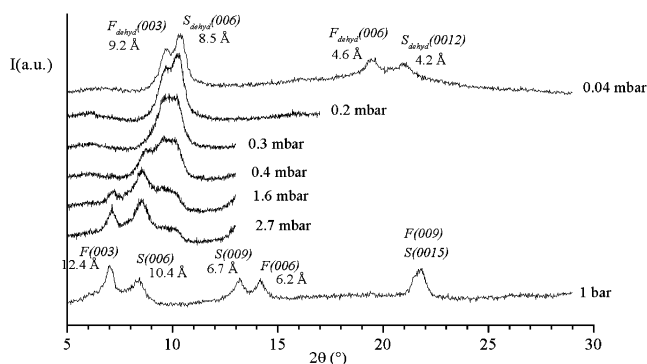

Figure 6. In situ X-ray powder diffraction data showing the course of drying under vacuum for $[Zn_2Cr-Cl]$ exchanged with tartrate anions for $A^{2-}/Cr^{3+} = 0.5$.
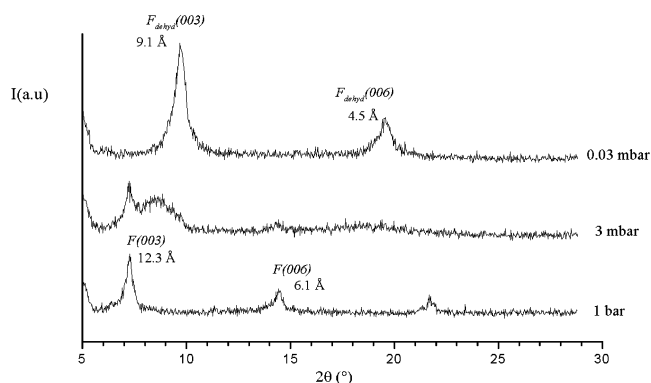

Figure 7. In situ X-ray powder diffraction data showing the course of drying under vacuum for $[Zn_2Cr-tartrate]$ fully exchanged with tartrate anions.

dried at room temperature under vacuum. A significant decrease of the d spacings compared to the wet state is observed because of the removal of interlayer water molecules. This was checked by conducting drying tests on the above sample freshly prepared, as well as on the fully exchanged materials as a single phase. The pattern of the wet samples, together with those of the samples after drying under different reduced pressures, is presented in Figures 6 and 7 (low 2θ range). In wet conditions, the basal spacings are equal to those obtained in aqueous suspensions. The progressive vacuum-drying results in a gradual decrease of the interlayer distances of both compounds. In a highly dehydrated state, the d_{003} spacing of F phase is 9.18 Å and that of the S phase is 16.8 ($3d_{009}$) Å. The corresponding contractions of the interlamellar distance are 3.2 and 2.9 Å,

respectively. These values are very close to the contraction obtained under thermal treatment for [Zn$_2$Cr−tartrate] at 150 °C, 2.9 Å,[14] which was interpreted as a reorientation of the tartrate anions in a flat position after the removal of interlayer water molecules, allowing the creation of hydrogen bonds between alcohol groups and the host. A similar reorientation of the tartrate anions is thus expected here, in both first and second-staged compounds.

Conclusion

According to the theoretical models, staging in LDHs should not be observed owing to the rigidity of the layers. Yet, phenomena related to staging have been reported recently for LiAl$_2$(OH)$_6$Cl·2H$_2$O during the intercalation of a series of dicarboxylate anions, as well as for MgAl-based LDH by direct synthesis of mixed hydroxide/azobenzene intercalates and for the exchange of interlayer terephthalate anions by chloride and nitrate anions. However, because of the scarcity of staging in the LDH system or the lack of experimental evidence, the reasons it takes place have not been clearly established yet.

In the present work, we examined the exchange of chloride anions in [Zn$_2$Al−Cl], [Zn$_2$Cr−Cl], and [Cu$_2$Cr−Cl] by tartrate and succinate anions. Monitoring the process in situ using energy-dispersive X-ray diffraction reveals the formation of second-stage intermediates caused by the filling of every second layer in all cases. Depending on the nature of the organic anion, two exchange pathways are observed. For tartrate anions, their complexing power would impede the exchange process; the fully exchanged material is not detected until the intermediate has gone through its maximum and the chloride precursor has disappeared completely. For succinate exchange, the final state of intercalation and the second-stage intermediate simultaneously appear, which might indicate that the actual reaction pathway involves an additional reaction of the fully exchanged materials with the chloride precursors.

Under vacuum-drying, [Zn$_2$−Cr] tartrate second-stage intermediate undergoes a contraction of the interlamellar space similar to that reported for the tartrate fully exchanged material but under moderate thermal treatment (80 °C). This is attributed to a reorientation of tartrate anions in a flat position after the removal of interlayer water molecules allowing the creation of hydrogen bonds between alcohol groups and the host.

Regarding the occurrence of staging in the intercalation of LDH, our results demonstrate that staging does not require a structural order of the host and is not affected by the corrugation of [Cu$_2$Cr−Cl] hydroxide layers. Furthermore, staging here is not believed to arise from two orientations of tartrate or succinate anions. Staging is not associated with the formation of bipolar two-nanolayer tactoids; this mechanism is not compatible with an exchange process and is inconsistent with the large size of the present chloride precursors particles (∼1 μm). Because staging has never been observed with mixed inorganic anion-exchanged LDH, one may think that it is a peculiarity of organic/inorganic systems and would result from the hydrophobic binding effect of the organic part. Yet, the question of second-order staging remains because no higher-order staging has been detected in a LDH system so far. In situ time-resolved energy-dispersive X-ray diffraction experiments are underway to determine the kinetics of these intercalation reactions.

References and Notes

(1) (a) Shaw, B. R.; Creasy, K. E. *J. Electroanal. Chem.* **1988**, *243*, 209. (b) Qiu, J.; Villemure, G. *J. Electroanal. Chem.* **1997**, *428*, 165. (c) Sugimoto, A.; Ishida, S.; Hanawa, K. *J. Electrochem. Soc.* **1999**, *146*, 1251. (d) Vaccari, A. *Appl. Clay Sci.* **1999**, *14*, 161.

(2) Leroux, F.; Besse, J.-P. *Chem. Mater.* **2001**, *13*, 3507 and references therein.

(3) Rudorff, W. *Z. Phys. Chem.* **1940**, *45*, 42.

(4) Schon, J. C.; Alder, D.; Dresselhaus, G. *J. Phys. C: Solid State Phys.* **1988**, *21*, 5595.

(5) Solin, S. A. *J. Mol. Catal.* **1987**, *27*, 293.

(6) Daumas, N.; Herold, A. *C. R. Acad. Sci. Paris C* **1969**, *268*, 373.

(7) O'Hare, D.; Evans, J. S. O.; Fogg, A. M.; O'Brien, S. *Polyhedron* **2000**, *19*, 297 and references therein.

(8) (a) Fogg, A. M.; Dunn, J. S.; O'Hare, D. *Chem. Mater.* **1998**, *10*, 356. (b) Thiel, J. P.; Chiang, C. K.; Poeppelmeier, K. R. *Chem. Mater.* **1993**, *5*, 297. (c) Besserguenev, A. V.; Fogg, A. M.; Price, S. J.; Francis, R. J.; O'Hare, D.; Isupov, V. P.; Tolochko, B. P. *Chem. Mater.* **1997**, *9*, 241.

(9) Iyi, N.; Kurashima, K.; Fujita, T. *Chem. Mater.* **2002**, *14*, 583.

(10) Kaneyoshi, M.; Jones, W. *Chem. Phys. Lett.* **1998**, *296*, 183.

(11) Ijdo, W. L.; Pinnavaia, T. J. *J. Solid State Chem.* **1998**, *139*, 281.

(12) Roussel, H.; Briois, V.; Elkaim, E.; de Roy, A.; Besse, J.-P. *J. Phys. Chem. B* **2000**, *104*, 5915.

(13) (a) Meyn, M.; Beneke, K.; Lagaly G. *Inorg. Chem.* **1990**, *29*, 5201. (b) Naumov, D. Y.; Podberezskaya, N. V.; Boldyreva, E. V.; Virovets, A. V. *J. Struct. Chem.*, **1996**, *37*, 480.

(14) Prevot, V.; Forano, C.; Besse, J.-P.; Abraham, F. *Inorg. Chem.* **1998**, *37*, 4293.

(15) Miyata, S. *Clays Clay Miner.* **1983**, *11*, 305.

(16) Villain, F.; Briois, V.; Castro, I.; Helary, C. Verdaguer, M. *Anal. Chem.* **1993**, *65*, 2545.

(17) De Roy, A.; Forano, C.; El Malki, K.; Besse J.-P. In *Synthesis of Microporous Materials*; Ocelli, M. L., Robson, H. E., Eds.; Van Nostrand Reinhold: New York, 1992; Vol. II, pp 108−169.

(18) Raki, L.; Rancourt, D. G.; Detellier, C. *Chem. Mater.* **1995**, *7*, 221.