

## Selective Anion-Exchange Properties of Second-Stage Layered Double Hydroxide Heterostructures

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The anion-exchange properties of second-stage  $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{Cl}_{0.5}(\text{succinate})_{0.25}\cdot n\text{H}_2\text{O}$  ( $\text{Zn}_2\text{Cr-Succ/Cl}$ ) and  $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{Cl}_{0.5}(\text{tartrate})_{0.25}\cdot n\text{H}_2\text{O}$  ( $\text{Zn}_2\text{Cr-Tart/Cl}$ ) materials were investigated by means of time-resolved in situ energy-dispersive X-ray diffraction (EDXRD). Selective anion-exchange reactions were observed that were a result of the segregation between organic and inorganic anions. Indeed, the reaction of  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/Cl}$  second-stage compounds with either fluoride or adipate anions initially occurs with preferential replacement of the hydrophilic Cl ion with F or replacement of the hydrophobic succinate or tartrate anions with adipate; this leads to the formation of new second-stage intermediates  $\text{Zn}_2\text{Cr-Succ/F}$  and  $\text{Zn}_2\text{Cr-Tart/F}$  or  $\text{Zn}_2\text{Cr-Adip/Cl}$ . The formation of such heterostructures offers new perspectives for LDH intercalation chemistry, particularly in the direction of multifunctional materials.

### Introduction

The study of multifunctional hybrid materials combining organic and inorganic structures is an emerging research area that offers numerous scientific and technological benefits. In this respect, hybrid nanostructures based on layered double hydroxides (LDH) have attracted much attention. LDHs constitute a unique class of lamellar compounds with a highly tunable metal hydroxide layer composition coupled with a wide choice of interlayer anions between the positively charged layers.<sup>1</sup> They are generally described by the formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2][\text{A}^{m-}_{x/m}\cdot n\text{H}_2\text{O}]$ , abbreviated hereafter as  $\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x\text{-A}^{m-}$ , where  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  are di- and trivalent cations, respectively, and  $\text{A}^{m-}$  is one or more of a wide variety of anions. A large number of hybrid LDH materials have been reported and numerous potential applications identified.<sup>2</sup> These include applications as catalysts, electrochemical sensors, adsorbents, and stabilizers for polymers.<sup>2,3</sup>

The staging phenomenon for LDH materials, recently discovered by O'Hare et al.,<sup>1,4</sup> conceptually opens new possibilities for tailoring hybrid LDH nanostructures. By means of time-resolved, in situ energy dispersive X-ray diffraction (EDXRD) experiments, these authors have shown the formation of crystalline second-stage phases during the intercalation of a variety of carboxylate anions into  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot\text{H}_2\text{O}$ . These phases have alternate interlayer regions

occupied by different anionic species. A few other studies have since shown the formation of second-stage materials for other LDH compositions. For instance, Iyi et al. have reported the formation of mixed hydroxide/azobenzene intercalates of  $\text{Mg}_2\text{Al}$  LDH, obtained via a coprecipitation route.<sup>5</sup> In addition, Pisson et al. have reported staging during the intercalation of tartrate and succinate anions into  $[\text{Zn}_2\text{-Al}(\text{OH})_6]\text{Cl}\cdot n\text{H}_2\text{O}$ ,  $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{Cl}\cdot n\text{H}_2\text{O}$  and  $[\text{Cu}_2\text{Cr}(\text{OH})_6\text{-Cl}]\cdot n\text{H}_2\text{O}$ .<sup>6</sup> A similar mixing of gallery organic and inorganic ions has been reported on a small number of occasions in fluorohectorite clay systems.<sup>7</sup> The formation of such heterostructures is of major interest for future developments in LDH intercalation chemistry, with the ultimate objective of preparing multifunctional materials. Combining the hydrophobic and hydrophilic properties of organic and inorganic LDH intercalates in a single heterostructured phase will produce amphiphilic materials, which may have novel ion-exchange properties.

In a previous work, we examined the exchange process of a series of LDH molecules by means of EDXRD and showed the formation of second-stage intermediates;<sup>6</sup> in the present study, we aimed to go further by investigating the exchange properties of these second-stage intermediate phases, i.e.,  $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{Cl}_{0.5}(\text{succinate})_{0.25}\cdot n\text{H}_2\text{O}$  and  $[\text{Zn}_2\text{-Cr}(\text{OH})_6]\text{Cl}_{0.5}(\text{tartrate})_{0.25}\cdot n\text{H}_2\text{O}$ , abbreviated hereafter as  $\text{Zn}_2\text{-Cr-Succ/Cl}$  and  $\text{Zn}_2\text{-Cr-Tart/Cl}$ . An initial series of time-resolved EDXRD experiments was performed to determine the conditions of formation of the  $\text{Zn}_2\text{-Cr-Succ/Cl}$  and  $\text{Zn}_2\text{-Cr-Tart/Cl}$  compounds. The two second-stage materials were then separately treated with adipate and fluoride anions and the reactions followed in situ. Selective anion-exchange

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reactions were observed that were a result of the differences in the polarity of the interlayer spaces.

### Experimental Section

**Time-Resolved In Situ Energy-Dispersive X-ray Diffraction (EDXRD) Experiments.** Experiments were carried out on Station 16.4 of the U.K. Synchrotron Radiation Source at the Daresbury Laboratory using an experimental setup reported elsewhere.<sup>8</sup> This allowed us to observe  $d$ -spacings between 4 and 115 keV, which correspond to  $d$  values in the range of ca. 109–3.8 Å. For the present study, the main information is in the range 20–3.8 Å.

The reactions were conducted in glass ampules contained within a temperature-controlled block; individual spectra were collected at a fixed detector angle of  $2\theta = 1.625^\circ$ , with acquisition times ranging from 10 to 60 s. In a typical experiment, a solution of the guest species (at a concentration of 0.2 M for tartrate/ $^-O_2C(CHOH)_2CO_2^-$  and succinate/ $^-O_2C(CH_2)_2CO_2^-$  anions, 0.15 or 0.2 M for adipate/ $^-O_2C(CH_2)_4CO_2^-$  anions, and 0.4 M for fluoride anions) was added dropwise to 10 mL of a suspension of the LDH (25 g L<sup>-1</sup>) at a rate of 0.046 or 0.059 mL min<sup>-1</sup> using a syringe pump. Spectra were thus recorded at different anion/LDH ratios in solution converted into theoretical exchange rates expressed in AEC (anionic exchange capacity).

In a previous study, we examined the exchange behavior of a series of Zn<sub>2</sub>Al-Cl, Zn<sub>2</sub>Cr-Cl, and Cu<sub>2</sub>Cr-Cl LDH molecules in EDXRD conditions.<sup>6</sup> A better crystallinity was observed in the case of the Zn<sub>2</sub>Cr system, which led us to choose this composition for the present work; the synthesis and chemical composition of Zn<sub>2</sub>Cr-Cl are reported elsewhere (also see the Supporting Information).<sup>6</sup>

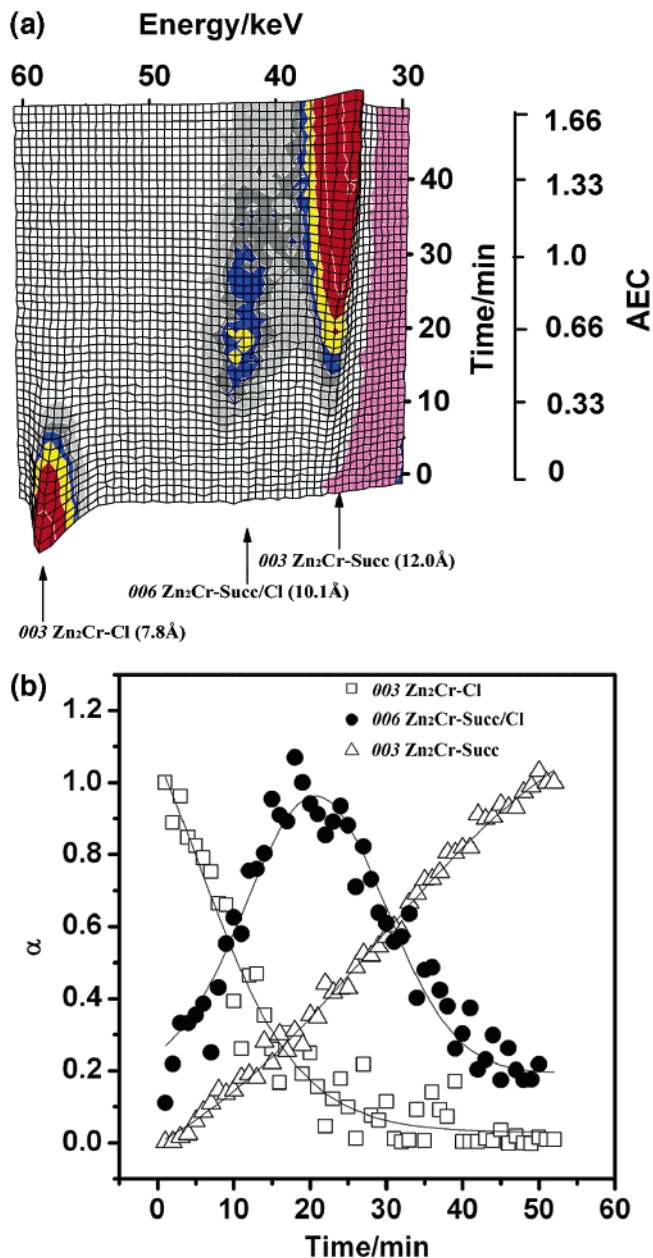
**Data Analysis.** An automated Gaussian fitting routine was used to obtain the peak areas of the Bragg reflections.<sup>9</sup> These values are then converted to the extent of reaction at time  $t$ , with  $t$  defined as  $\alpha(t) = I_{hkl}(t)/I_{hkl}(\max)$ , where  $I_{hkl}(t)$  is the area of a given peak at time  $t$ , and  $I_{hkl}(\max)$  is the maximum area of this peak.

**Powder X-ray Diffraction.** Powder X-ray diffraction patterns were recorded on an X'Pert Pro Philips diffractometer using Cu K $\alpha$  radiation. Divergence and receiving slits were 1/16° and 1 mm, respectively. Data were collected in a step scan mode between 2.0 and 70°  $2\theta$ , with a step size of 0.03°  $2\theta$  and a counting time of 10 s/step.

### Results and Discussion

**Formation of Second-Stage Zn<sub>2</sub>Cr-Succ/Cl and Zn<sub>2</sub>Cr-Tart/Cl Materials.** Plots showing the reaction of Zn<sub>2</sub>Cr-Cl with succinate or tartrate anions are presented in Figures 1 and 2, respectively. It is important to note that these exchange reactions occur very rapidly in a few minutes at room temperature, so in order to study these reactions in detail, it was necessary to add the anion solution in a dropwise manner. However, this experimental setup prevents a full quantitative kinetic analysis of the data.

In both cases, two reaction products were identified during the exchange process. The reflections were indexed on the basis of a hexagonal unit cell with the  $R\bar{3}m$  rhombohedral symmetry commonly observed in LDH systems. EDXRD data show three Bragg reflections at  $d$ -spacing  $\approx 7.8$  Å (host

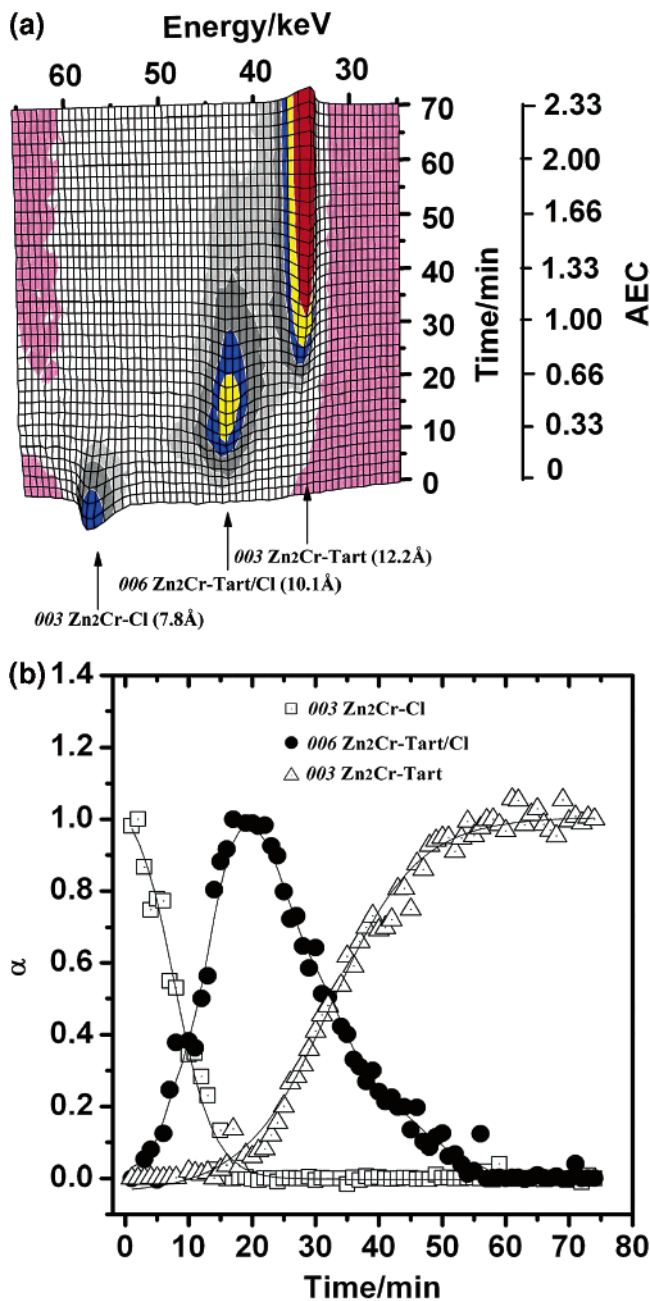


**Figure 1.** EDXRD data showing the course of the exchange reaction of Zn<sub>2</sub>Cr-Cl with succinate ( $^-O_2C(CH_2)_2CO_2^-$ ) at room temperature. (a) Three-dimensional stacked plot showing reflections attributable to the host, a second-stage intermediate phase, and the fully exchanged product. (b) Extent of reaction vs time curves showing the evolution of Zn<sub>2</sub>Cr-Cl 003, Zn<sub>2</sub>Cr-Succ/Cl 006, and Zn<sub>2</sub>Cr-Succ 003 Bragg reflections as a function of time; the succinate anion solution (0.2 M) was added at a rate of 0.059 mL min<sup>-1</sup>. Individual spectra were collected with an acquisition time of 60 s. The amount of guest anions added in solution is converted into theoretical anion exchange rates (AEC), given on the right scale.

Zn<sub>2</sub>Cr-Cl 003), 10.1 Å (second-stage Zn<sub>2</sub>Cr-Succ/Cl or Zn<sub>2</sub>Cr-Tart/Cl 006), and 12.0/12.2 Å (first-stage products corresponding to the fully exchanged phases Zn<sub>2</sub>Cr-Succ or Zn<sub>2</sub>Cr-Tart 003). The Zn<sub>2</sub>Cr-Succ/Cl or Zn<sub>2</sub>Cr-Tart/Cl second-stage materials have alternate interlayers occupied by chloride anions and either succinate or tartrate anions.  $d_{003}$  of such heterostructures is thus equal to the sum of  $d_{003}$  of the host (7.8 Å) and  $d_{003}$  of the first-stage products (12.0 Å for succinate, 12.2 Å for tartrate), leading to  $d_{003} = 19.8$  Å for Zn<sub>2</sub>Cr-Succ/Cl and 20.0 Å for Zn<sub>2</sub>Cr-Tart/Cl. In the present study, the experimental setup did not allow us to observe the 003 reflection of Zn<sub>2</sub>Cr-Succ/Cl or Zn<sub>2</sub>Cr-Tart/Cl phases.

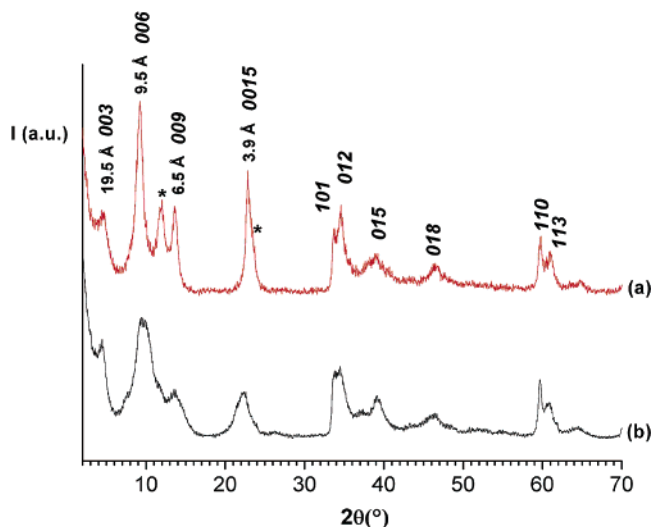
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**Figure 2.** EDXRD data for the reaction of  $\text{Zn}_2\text{Cr-Cl}$  with tartrate ( $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ) at room temperature. (a) Three-dimensional stacked plot and (b) extent of reaction vs time curves showing the evolution of  $\text{Zn}_2\text{Cr-Cl}$  003,  $\text{Zn}_2\text{Cr-Tart/Cl}$  006, and  $\text{Zn}_2\text{Cr-Tart}$  003 Bragg reflections as a function of time; the tartrate anion solution (0.2 M) was added at a rate of  $0.059 \text{ mL min}^{-1}$ .

Only the 006 reflections are visible, and the expected values are  $d_{006} = 9.9 \text{ \AA}$  for  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $10.0 \text{ \AA}$  for  $\text{Zn}_2\text{Cr-Tart/Cl}$ . The extent of the reaction ( $\alpha$ ) versus time curves are given in Figures 1b and 2b. As demonstrated elsewhere, such plots may further confirm the formation of  $\text{Zn}_2\text{Cr-Succ/Cl}$  or  $\text{Zn}_2\text{Cr-Tart/Cl}$  intermediates.<sup>4a</sup> Indeed, the fact that the  $\alpha(t)$  curves for the host and first-stage products cross at  $\approx 0$  indicates the presence of an intermediate phase. Besides, the crossing at  $\alpha \approx 0.5$  of  $\alpha(t)$  curves for the host and the intermediate, as well as for the intermediate and the product, are indicative of a two-step process with initial conversion of the host to the second-stage compound, followed by conversion of this material to the product. As can be seen in



**Figure 3.** X-ray powder diffraction patterns for the second-stage phases: (a)  $\text{Zn}_2\text{Cr-Succ/Cl}$  and (b)  $\text{Zn}_2\text{Cr-Tart/Cl}$ . Reflections marked with an asterisk correspond to the  $\text{Zn}_2\text{Cr-Cl}$  host.

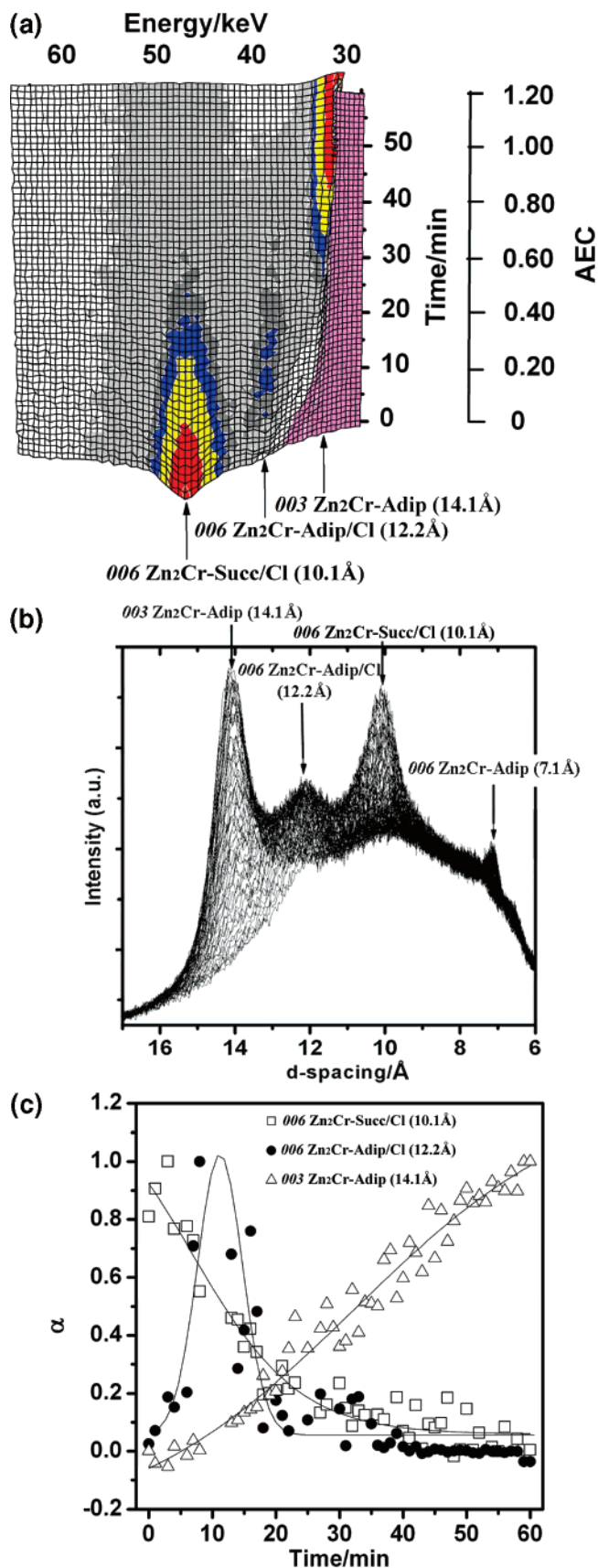
Figure 2b, the exchange reaction with tartrate anions obeys such a consecutive process. On the other hand, for the exchange reaction with succinate anions, the  $\alpha(t)$  curves for the host, and the first-stage products cross at  $\alpha \approx 0.3$  (Figure 1b), suggesting parallel processes with a route probably going through the intermediate, as well as a direct transformation of the host. These results are consistent with those we previously obtained; the better quality of the present data allows us to confirm the trends highlighted in this previous work, in particular the existence of different exchange pathways depending on the nature of the organic anions.<sup>6</sup>

#### Anion-Exchange Properties of Second-Stage Materials.

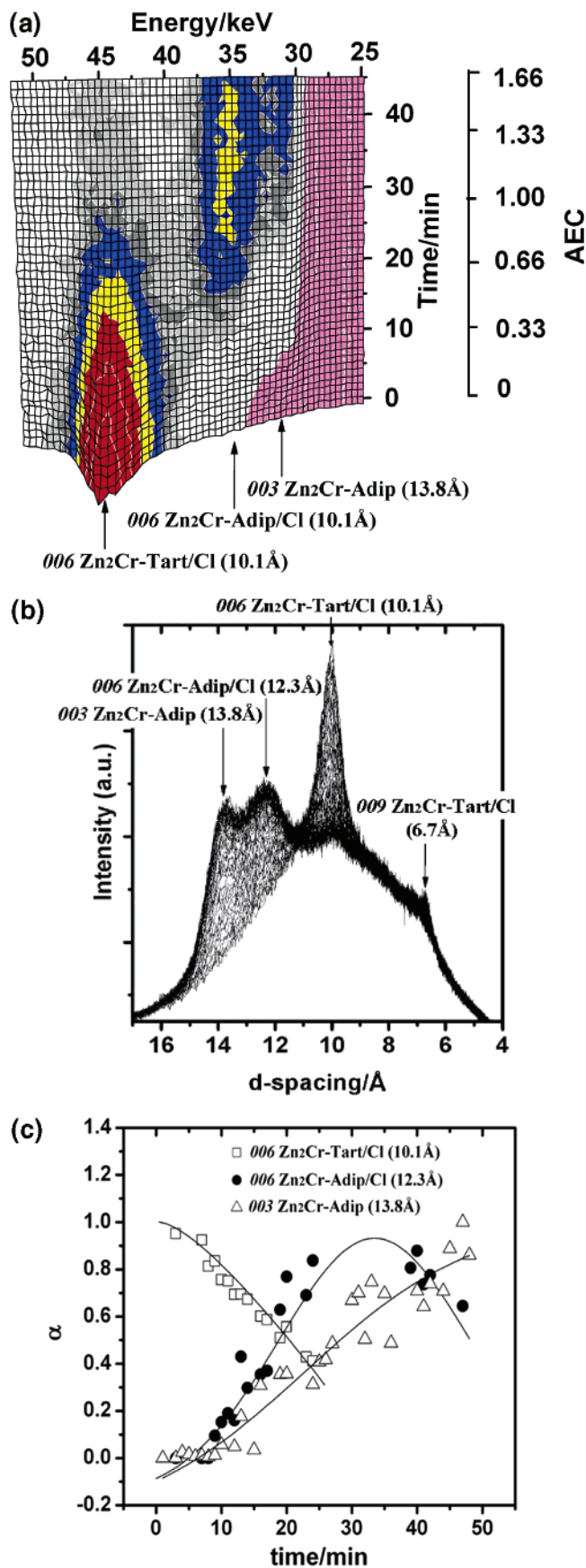
For the in situ study of the anion-exchange properties of  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/Cl}$ , both second-stage phases were first prepared in the laboratory by repeating the EDXRD experiments described above and quenching the reactions when solely the second-stage phases are present, i.e., at a reaction time corresponding to the crossing point of  $\alpha(t)$  curves of the host and the product, where the concentration of the intermediate is expected to be greatest.<sup>10</sup> The powder X-ray diffraction patterns of the quenched materials are shown in Figure 3. As can be seen, the  $\text{Zn}_2\text{Cr-Succ/Cl}$  sample is not a pure phase but consists of a mixture of  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Cl}$ . It is worthwhile to note that with reaction time scales on the order of 1–2 min, it is difficult to isolate second-stage intermediates, and products quenched after drying do not necessarily reflect the reaction matrix. In contrast,  $\text{Zn}_2\text{Cr-Tart/Cl}$  appears as a pure phase sample. Another very important point is the detection of 003 reflections at ca.  $19.5 \text{ \AA}$  in each case, providing irrefutable proof that second-stage materials are formed. The as-prepared second-stage materials were then resuspended in water ( $25.0 \text{ g L}^{-1}$ ), and EDXRD experiments were performed to follow the exchange reactions with adipate and fluoride anions, under the same conditions as those described above.

Plots showing the time evolution of the exchange reactions with adipate anions are presented in Figures 4 and 5 for  $\text{Zn}_2\text{-}$

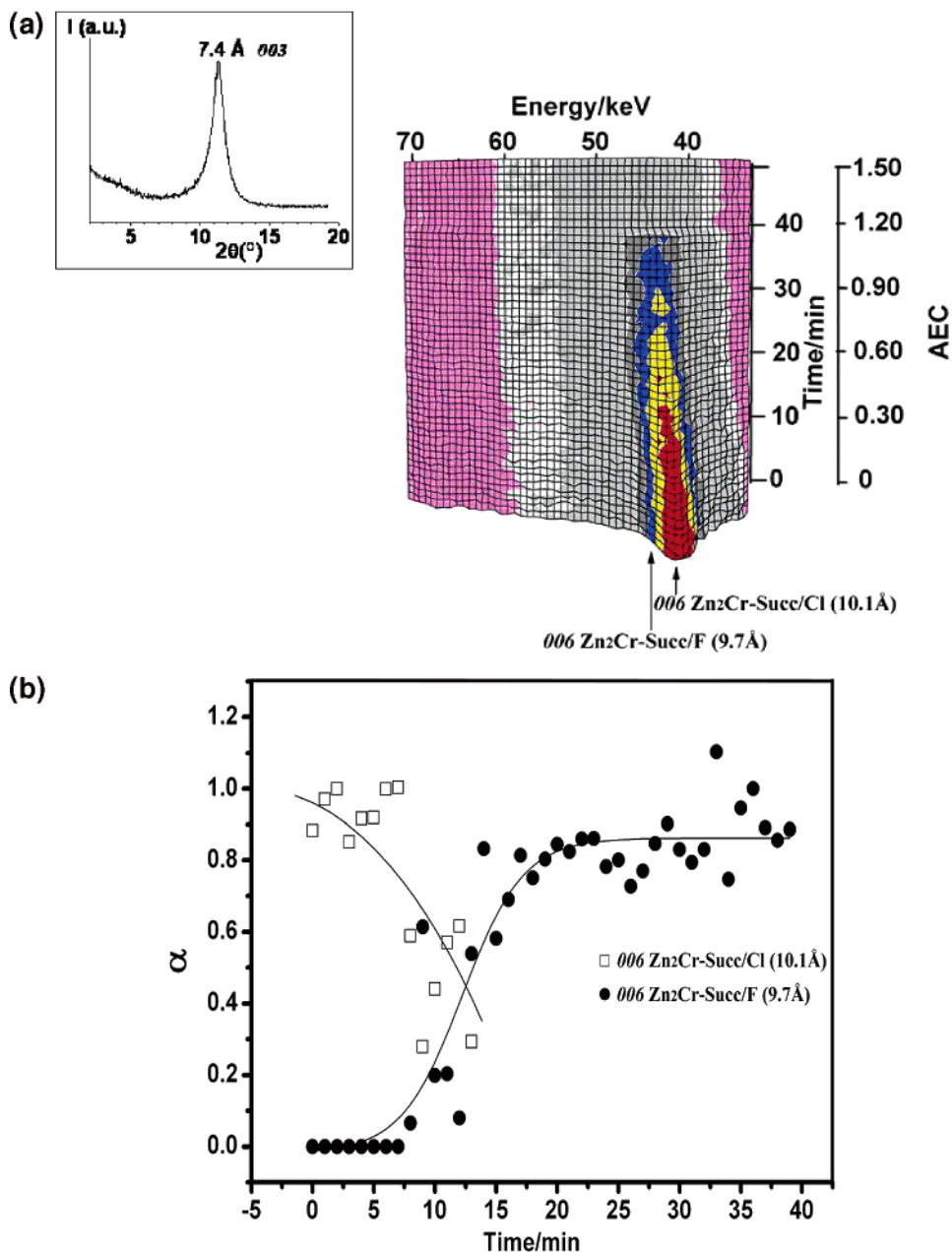
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**Figure 4.** EDXRD data showing the course of the exchange reaction of adipate ( $\text{C}_6\text{H}_4(\text{CO}_2^-)_2$ ) with Zn<sub>2</sub>Cr-Succ/Cl at room temperature. (a) Three-dimensional stacked plot, (b) stacked diffraction patterns collected at different stages of the reaction, and (c) vs. time curves showing the evolution of Zn<sub>2</sub>Cr-Succ/Cl 006, Zn<sub>2</sub>Cr-Adip/Cl 006, and Zn<sub>2</sub>Cr-Adip 003 Bragg reflections as a function of time; the adipate anion solution (0.15 M) was added at a rate of 0.046 mL min<sup>-1</sup>.



**Figure 5.** EDXRD data showing the course of the exchange reaction of adipate with Zn<sub>2</sub>Cr-Tart/Cl at 55 °C. (a) Three-dimensional stacked plot showing the evolution of Zn<sub>2</sub>Cr-Tart/Cl 006, Zn<sub>2</sub>Cr-Adip/Cl 006, and Zn<sub>2</sub>Cr-Adip 003 Bragg reflections as a function of time; the adipate solution (0.2 M) was added at a rate of 0.059 mL min<sup>-1</sup>. (b) Two-dimensional stacked plots showing the same. (c) Extent of reaction vs time curves.



**Figure 6.** Time-resolved diffraction data showing the course of the reaction of fluoride with Zn<sub>2</sub>Cr-Succ/Cl at room temperature. (a) Three-dimensional stacked plot showing the evolution of Zn<sub>2</sub>Cr-Succ/Cl 006 and Zn<sub>2</sub>Cr-Adip/F 006 Bragg reflections as a function of time; the fluoride anion solution (0.4 M) was added at a rate of 0.046 mL min<sup>-1</sup>. (b) Extent of reaction vs time curves. Inset figure gives the powder X-ray diffraction pattern of the final solid recovered after centrifugation and drying.

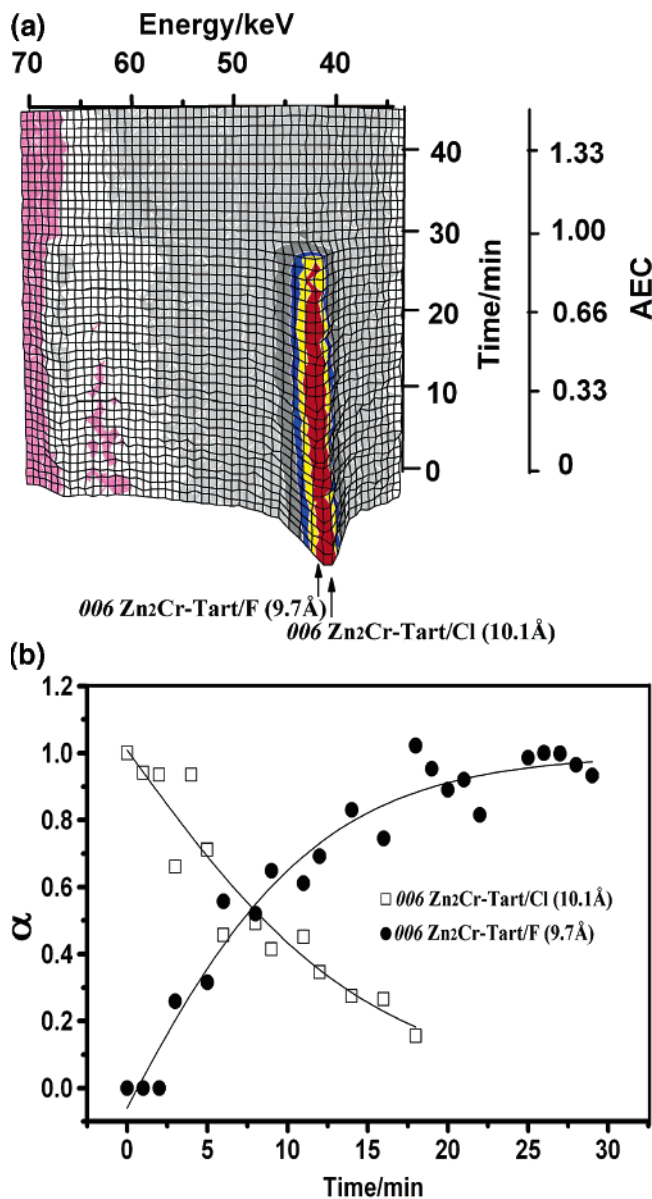
Cr-Succ/Cl and Zn<sub>2</sub>Cr-Tart/Cl, respectively, and those corresponding to the exchange with fluoride anions are presented in Figures 6 and 7. In all cases, the reactions are observed to proceed in two steps and new second-stage intermediate phases are identified that result from the selective replacement of either succinate or tartrate anions by adipate anions, or Cl<sup>-</sup> anions by F<sup>-</sup> anions.

*Exchange Reactions with Adipate Anions.* For the exchange reaction of adipate anions with Zn<sub>2</sub>Cr-Succ/Cl host

(panels a and b of Figures 4), a crystalline intermediate phase was detected at ca. 12.2 Å that can be assigned to a new second-stage intermediate, Zn<sub>2</sub>Cr-Adip/Cl. This phase has alternate layers occupied by chloride and adipate anions, and hence has a predicted  $d_{003} = 7.8 + 14.1 = 21.9$  Å, and hence a  $d_{006}$  of ca. 11 Å. This latter value is slightly different from that observed (12.2 Å), but the low crystallinity of Zn<sub>2</sub>Cr-Adip/Cl intermediate makes the determination of the exact position of the Bragg reflection rather difficult. Additionally, the poor crystallinity and the partial overlap between Bragg reflections complicate the integration of the diffraction intensities, thus explaining the relatively poor resolution for  $\alpha$ -time curves.

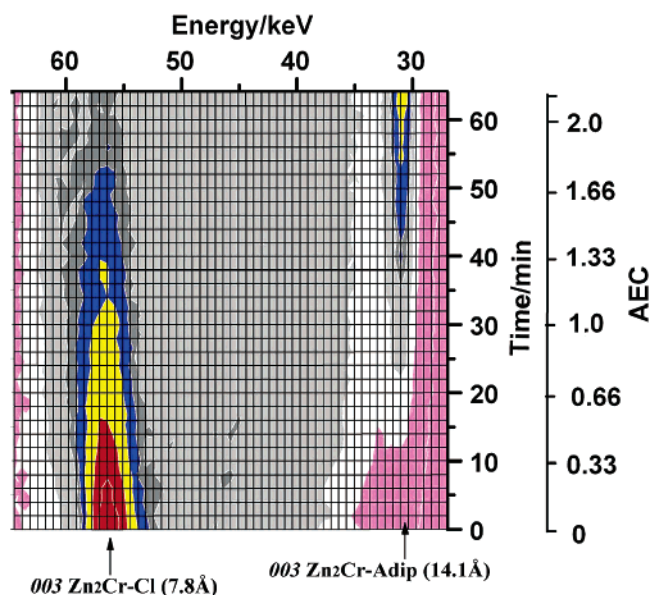
For the exchange reaction of adipate anions with the Zn<sub>2</sub>Cr-Tart/Cl host, the intermediate was initially very hard to

(11) In our first attempts, we successively monitored in one experiment the formation of Zn<sub>2</sub>Cr-Succ/Cl or Zn<sub>2</sub>Cr-Tart/Cl intermediates followed by the exchange reactions with fluoride or adipate anions. Yet, under these conditions, the crystallinity of the system decreased dramatically and it was impossible to analyze the data. This failure can be attributed to a combination of factors: first, a dilution factor, which makes detection difficult, and second, a competition between anions in solution, which may hinder their intercalation.



**Figure 7.** EDXRD data for the reaction of fluoride with  $\text{Zn}_2\text{Cr-Tart/Cl}$  at room temperature. (a) Three-dimensional stacked plot showing the evolution of  $\text{Zn}_2\text{Cr-Tart/Cl}$   $006$  and  $\text{Zn}_2\text{Cr-Adip/F}$   $006$  Bragg reflections as a function of time; the fluoride anion solution (0.4 M) was added at a rate of  $0.059 \text{ mL min}^{-1}$ . (b) Extent of reaction vs time curves.

observe and only the fact that the extent of the reaction vs time curves of the  $\text{Zn}_2\text{Cr-Tart/Cl}$  host and  $\text{Zn}_2\text{Cr-Adip}$  product cross at  $\alpha \approx 0$  suggested the presence of an intermediate (results not shown). However, performing the reaction at  $55^\circ\text{C}$  allowed us to improve the detection and unequivocally observe the growth of a Bragg reflection at the same distance as for the  $\text{Zn}_2\text{Cr-Succ/Cl}$  host, i.e.,  $12.2 \text{ \AA}$  (panels a and b of Figure 5). This coincidence in position strongly suggests a similar composition for the intermediate phase, i.e.,  $\text{Zn}_2\text{Cr-Adip/Cl}$ , in both cases. However, the effect of temperature in the case of the  $\text{Zn}_2\text{Cr-Tart/Cl}$  host reveals differences in reactivity between  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/Cl}$  compounds, probably with a higher activation energy for the exchange reaction of tartrate with adipate than that of succinate. Additionally, there is a difference in the induction time, before the reaction begins. Indeed, for the  $\text{Zn}_2\text{Cr-Tart/Cl}$  host, the  $\text{Zn}_2\text{Cr-Adip/Cl}$  intermediate is not



**Figure 8.** EDXRD data for the exchange reaction between  $\text{Zn}_2\text{Cr-Cl}$  and adipate anions at room temperature showing the evolution of  $\text{Zn}_2\text{Cr-Cl}$   $003$  and  $\text{Zn}_2\text{Cr-Adip}$   $003$  Bragg reflections with time. The adipate anion solution (0.2 M) was added at a rate of  $0.059 \text{ mL min}^{-1}$ .

detected until the theoretical exchange rate has reached a value of ca. 0.6, whereas for the  $\text{Zn}_2\text{Cr-Succ/Cl}$  host,  $\text{Zn}_2\text{Cr-Adip/Cl}$  is detected at the initial stages of adipate addition, at a theoretical exchange rate of ca. 0.15. The conditions for the appearance of the  $\text{Zn}_2\text{Cr-Adip}$  product are also different, with the coexistence of  $\text{Zn}_2\text{Cr-Adip/Cl}$  and  $\text{Zn}_2\text{Cr-Adip}$  in the case of the  $\text{Zn}_2\text{Cr-Tart/Cl}$  host, whereas  $\text{Zn}_2\text{Cr-Adip}$  is not observed until  $\text{Zn}_2\text{Cr-Adip/Cl}$  has disappeared in the case of the  $\text{Zn}_2\text{Cr-Succ/Cl}$  host. The persistence of the  $\text{Zn}_2\text{Cr-Adip/Cl}$  intermediate in the former case might indicate a random filling of the Cl-containing layers after alternate layers have been exchanged with adipate anions. Conversely, for the  $\text{Zn}_2\text{Cr-Succ/Cl}$  host, the direct transformation from the  $\text{Zn}_2\text{Cr-Adip/Cl}$  intermediate to the  $\text{Zn}_2\text{Cr-Adip}$  product would arise from an ordered replacement of the Cl-containing layers, supported by the fact that the corresponding  $\alpha$  vs time curves cross at  $\alpha = 0.5$  (Figure 5c). Another explanation could be differences in the anion-exchange affinities, the exchange between tartrate and adipate anions being energetically less favorable than the exchange between succinate and adipate anions; this is consistent with the effect of the temperature showing that the activation energy is higher in the former case.

**Exchange Reactions with Fluoride Anions.** For the exchange reactions with fluoride anions (Figures 6 and 7 for  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/Cl}$ , respectively), a gradual displacement of the  $006$  reflection of  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/Cl}$  hosts from 10.1 to  $9.7 \text{ \AA}$  is observed in each case. This is in total agreement with the formation of new second-stage phases,  $\text{Zn}_2\text{Cr-Succ/F}$  and  $\text{Zn}_2\text{Cr-Tart/F}$ , both resulting from the replacement of  $\text{Cl}^-$  by  $\text{F}^-$  anions in  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/Cl}$ , respectively. Because of the small difference between the interlamellar distances for chloride ( $7.8 \text{ \AA}$ ) and fluoride ( $7.4 \text{ \AA}$ ) anions, only a small displacement of the  $006$  Bragg reflection of the second-stage phases to lower  $d$  values is expected upon the exchange of chloride by fluoride. The  $\text{Zn}_2\text{Cr-Succ/F}$  intermediate therefore has a

predicted  $d_{003} = 12.1 + 7.4 = 19.6$  Å, leading to a  $d_{006}$  of 9.8 Å; the same calculation for  $\text{Zn}_2\text{Cr-Tart/F}$  gives  $d_{006} = 9.9$  Å. This is in excellent agreement with the EDXRD data. A deconvolution of the EDXRD patterns in the range 9–11 Å (by considering two contributions centered at 10.1 and 9.7 Å, attributed to  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Succ/F}$  or  $\text{Zn}_2\text{Cr-Tart/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/F}$ ), allow us to draw the  $\alpha(t)$  curves presented in Figures 6b and 7b. Again, the crossing of these curves at  $\alpha \approx 0.5$  is consistent with a direct conversion of  $\text{Zn}_2\text{Cr-Succ/Cl}$  or  $\text{Zn}_2\text{Cr-Tart/Cl}$  hosts to  $\text{Zn}_2\text{Cr-Succ/F}$  or  $\text{Zn}_2\text{Cr-Tart/F}$  intermediates. In both cases, for a theoretical exchange rate approaching the anion-exchange capacity, the intermediate phase disappears. The fully exchanged phase  $\text{Zn}_2\text{Cr-F}$  with  $d_{003} = 7.4$  Å is not observed, probably because it is too poorly crystalline and cannot be resolved. Nevertheless, the powder XRD analysis of the final solid product recovered after centrifugation and drying unambiguously shows the formation of  $\text{Zn}_2\text{Cr-F}$  with the 003 Bragg reflection at ca. 7.4 Å (inset of Figure 6a).

### Conclusions

These results demonstrate a segregation between organic and inorganic anions, leading to selective exchange reactions

governed by this. The reaction of the second-stage compounds  $\text{Zn}_2\text{Cr-Succ/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/Cl}$  with either fluoride or adipate anions initially occurs with preferential replacement of the hydrophilic Cl ion with F or replacement of the hydrophobic succinate or tartrate anions with adipate. This result has major implications for the intercalation chemistry of LDHs. Another important point to note is that attempts to prepare  $\text{Zn}_2\text{Cr-Adip/Cl}$  and  $\text{Zn}_2\text{Cr-Tart/F}$  second-stage materials by direct synthesis failed. Indeed, no staging was observed for the exchange of chloride in  $\text{Zn}_2\text{Cr-Cl}$  by adipate (Figure 8) or for the exchange of tartrate by fluoride in  $\text{Zn}_2\text{Cr-Tart}$  (results not shown), which suggests that the present phases can be prepared starting only from second-stage structures such as  $\text{Zn}_2\text{Cr-Tart/Cl}$ .

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**Supporting Information Available:** Table of chemical compositions for  $\text{Zn}_2\text{Cr-Cl}$  precursor and the fully exchanged phases  $\text{Zn}_2\text{Cr-Succ}$  and  $\text{Zn}_2\text{Cr-Tart}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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