Identification and Quantification of Defects in the Cation Ordering in Mg/Al Layered Double Hydroxides

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Supporting Information



Figure S1. Pulse sequences of the solid-state NMR experiments used in this work. (a) NMR ${}^{1}H{}^{27}A1{}$ CP-MAS experiment. (b) Dipolar Homonuclear Homogeneous Hamiltonian (DH³) single-quantum-double quantum (DQ-SQ) ${}^{1}H{}^{-1}H$ experiment. This pulse sequence is identical to that of the refocused INADEQUATE experiment but used in a different context to probe internuclear distances rather than chemical bonds. (c) Symmetry-based ${}^{27}A1{}^{-27}A1{}$ dipolar recoupling $R2_{1}^{2}$ experiment. (d) Details of the $R2_{1}^{2} + R2_{1}^{-2}$ recoupling block used here for recoupling. The duration of the block is 4 rotor periods. Phases and pulse programs are available upon request to the authors.

Atom	Core- states	Local channel	r _{loc} (a.u.)	r _{nonloc} (a.u.)	<i>r_{aug}</i> (a.u.)	pseudopotential projectors	PAW projectors
Н		р	0.8	0.8	0.6	2x2s	2x2s
Ν	1s	d	1.4	1.6	0.8	2x2s, 2x2p	2x2s, 2x2p
0	1s	d	1.0	1.3	0.7	2x2s, 2x2p	2x2s, 2x2p
Mg	1s, 2s	d	1.6	2.0	1.4	2x3s,1x2p, 2x3p	2x3s, 1x2p, 2x3p, 2x3d
Al	1s, 2s,2p	d	2.0	2.0	1.7	2x3s, 2x3p	2x3s, 2x3p, 2x3d

Table S1. Description of pseudopotentials used for planewave-based DFT calculations.

Where r_{loc} is the pseudisation radius for the local component of the pseudopotential, r_{nonloc} is the pseudisation radius for the non-local components of the pseudopotential, and r_{aug} is the pseudisation radius for the charge augmentation functions.

The corresponding castep on-the-fly strings used to generate these potentials are:

H 1|0.8|0.8|0.6|2|6|8|10(qc=6) N 2|1.4|1.6|0.8|7|9|10|20:21 O 2|1.0|1.3|0.7|13|16|18|20:21(qc=7) Mg 2|1.6|2|1.4|6|7|8|30NH:21U:31UU:32LGG(qc=4.5) Al 2|2.0|2.0|1.7|1|2|3|30:31:32LGG(qc=3) Cadars S. et al, Defects in the Cation Ordering in Mg/Al Layered Double Hydroxides, Supporting Information



Figure S2. (a) Transmission electron micrograph (TEM) of the LDH material with Mg/Al molar ratio of 2 co-precipitated at constant pH = 10 from the nitrate metal salts. The image reveals a well crystallized material with hexagonal morphology of the particles. Their mean size is in the range from 80 to 120 nm. Some particles oriented perpendicularly to the basal plane show 3 to 5 superimposed sheets. The basal spacing is in agreement with that determined by XRD. (b) X-ray diffractograms collected for samples Mg/Al-*y* with y = 2.5 (blue), 3.0 (red), and 3.5 (green).

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Effects of the basal spacing on calculated ¹H NMR chemical shifts. Systematic studies were conducted to monitor the effect of reducing the basal spacing in Mg/Al-2 ordered LDH with only Mg₂AlOH sites. We found that for basal spacings above 8 Å the intercalated NO₃⁻ anions are tilted with respect to the layer planes during geometry optimization. This leads to a distribution of H-bond distances to the framework hydroxyl groups, and a corresponding distribution of calculated ¹H chemical shifts (Figure S3). The standard deviation is as large as 2.3 ppm for c larger than 8.3 Å. In contrast, little dispersion of the calculated shifts was found for basal distances below 8.0 Å (standard deviations of 0.9 and 0.3 ppm for c = 7.9 and 7.3 Å, respectively). Thus, a large part of the observed dispersion of the calculated ¹H shifts in the ordered model likely results from a too large basal spacing, given that water molecules were not considered. However, when cation disorder is present, large dispersion of the ¹H chemical shifts calculated for AlMg₂OH moieties remains when the basal spacing is reduced (Figure S4). Thus, this chemical shift distribution cannot be attributed solely to the ability for the intercalated molecule to tilt with respect to the layers. DFT calculations conducted with a Mg/Al-2 disordered LDH model similar to that of Figure 3, but with basal spacings of 8.4 and 7.9 Å (instead of 8.81 Å), show a dispersion of ¹H chemical shifts (standard deviations of 1.2 and 1.3 ppm, respectively) still larger than the experimental ¹H NMR linewidth (0.6 ppm, fwhm) for AlMg₂OH moieties. Indeed, even for such low basal spacings, where the NO₃⁻ anions are forced to remain parallel to the layers for steric reasons, the range of H-bond length remains large because of distributed rotational (in the plane) and translational disorder of the NO_3^- anions.

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Figure S3. (a) Side and (b) top views of a structural model of LDH with intercalated nitrate compensation anions, Mg/Al = 2, and an ordered cation distribution, following the hypotheses described in the text, and obtained after geometry optimization in DFT with periodic boundary conditions. This structure is most efficiently described with a non-orthorhombic CM space group (a = b = 5.2897 Å, c = 9.4896 Å, $\alpha = \beta = 100.708^{\circ}$, $\gamma = 120^{\circ}$). After the geometry optimization, the orientation of the intercalated NO_3^- ions is no longer parallel to the MgAlOH layers, but instead tilted to form hydrogen bonds to the nearest OH groups. The ¹H NMR chemical shifts calculated for this structure spread across a range of 6 ppm, which is much larger than the experimental width of the Mg₂AlOH peak (0.6 ppm full width at half maximum(fwhm) from the deconvolution of the ${}^{1}H{}^{27}Al{}$ CP-MAS spectrum of Figure 2.b). This is presumably due to our neglecting the water molecules in the inter-layer space, since such water molecules, which are found to represent ca. 23% of the amount of ¹H present, as measured by NMR, *i.e.* approximately 1 water molecule for 10 framework hydroxyl groups, probably make it easier for most of them to form hydrogen-bonds, and could thus minimize the spread of ¹H chemical shifts. Interestingly, however, the center of mass of these calculated ¹H shifts: 2.9 ppm is not too far from the experimental shift of 3.8 ppm for such sites. At ambient temperature, dynamics of the nitrate would likely reduce this distribution around the center of mass.

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Figure S4. Effect of the inter-layer spacing on ¹H chemical shifts calculated for LDH models. (a) Isotropic ¹H shifts calculated for ordered LDH models similar to that of Figure S3, and using variable inter-layer distances. The average shift for each model is shown as a black diamond. Whereas the average shifts do not vary much with the inter-layer spacing, the scatter of the calculated value considerably increases when the inter-layer spacing increases above 8 Å. (b) Average isotropic ¹H chemical shifts calculated for disordered LDH model similar to that of Figure 3, with variable inter-layer distances. Bars indicate the standard deviation calculated for each type of site in every model. Dotted lines indicate the center of mass of each species, as observed in experimental ¹H NMR spectra. The effect of the inter-layer spacing in the scatter of calculated ¹H shifts is not as clear as for the ordered model, indicating that other effects contribute to the dispersion of ¹H shifts in this case.

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Figure S5. NMR 2D ²⁷Al double quantum-single quantum (DQ-SQ) correlation NMR spectrum of LDH sample Mg/Al-2, sheared from DQ-SQ to SQ-SQ. Spectra on the top and on the right side of the 2D spectrum are (in gray) the ²⁷Al Hahn echo spectrum, and (in black) the 1D DQ-filtered ²⁷Al spectrum of Figure 6b and 6c, respectively. This 2D spectrum confirms that the 1D spectrum of Figure 6c only displays selectively signals arising from pairs of adjacent ²⁷Al nuclei.

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Figure S6. NMR 2D ¹H-¹H DH³ DQ-SQ correlation spectra of LDH samples Mg/Al-*y* with y = 2.5 (a), 3.0 (b), and 3.5 (c). 1D spectra overlapped with the 2D spectra correspond to quantitative ¹H echo-MAS spectra (solid lines), T_2 -filtered ¹H spectra (dotted lines), and ¹H{²⁷Al} CP-MAS spectra collected with a contact time of 10 ms (dashed lines). All spectra were recorded at 17.6 Tesla, at the MAS frequency of 64 kHz. Conditions for all experiments are identical to those used for sample Mg/Al-2, and described in Experimental Section.

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Figure S7. NMR ²⁷Al Hahn echo spectra of LDH samples Mg/Al-*y* with y = 2.0 (in black, same spectrum as in Figure 6b), 2.5 (brown), 3.0 (red), and 3.5 (yellow), collected at 7.0 Telsa, at a MAS spinning frequency of 14 kHz. The magnification shows that no or very little four-coordinated aluminum (which could indicate phase segregation) is present. More importantly, increased distortions of the "ordered" ²⁷Al moieties at ca. 10 ppm are observed for Mg/Al ratios larger than 2, which cause additional broadening of this peak and its overlapping with the region corresponding to the more distorted environments attributed (at least in part) to adjacent Al moieties. Experimental conditions are the same as those used in the experiment shown in Figure 6b (and in black here), and are described in the Experimental Section.