

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/273792741>

Water Molecules in Hydrotalcite-like Layered Double Hydroxides: Interplay between the Hydration of the Anions and the Metal Hydroxide Layer: Water Molecules in Hydrotalcite-like La...

ARTICLE in ZEITSCHRIFT FÜR ANORGANISCHE CHEMIE · MARCH 2015

Impact Factor: 1.16 · DOI: 10.1002/zaac.201500065

READS

38

2 AUTHORS, INCLUDING:



Shivanna Marappa

Bangalore University

6 PUBLICATIONS 8 CITATIONS

SEE PROFILE

Water Molecules in Hydrotalcite-like Layered Double Hydroxides: Interplay between the Hydration of the Anions and the Metal Hydroxide Layer

Shivanna Marappa^[a] and P. Vishnu Kamath*^[a]

Keywords: Layered compounds; Anionic clays; Hydration; Magnesium; Aluminum

Abstract. Layered double hydroxides comprise positively charged metal hydroxide layers and intercalated anions. These materials are obtained from aqueous medium both in nature and in the laboratory. Consequently the layered double hydroxides include a considerable amount of water. The presented study was designed to determine the proportion of water associated with the hydration sphere of the anion as opposed to that of the metal hydroxide slab. Among the two differently bound water species observed in all layered double hydroxides, the weakly bound water is associated with the metal hydroxide

layer and is lost at 100 °C, whereas the strongly bound water is in the hydration sphere of the anion and is lost at higher temperatures (100 °C $\leq T \leq$ 250 °C). This is in contrast to the better known cationic clays, wherein all the intercalated water is generally found to be in the hydration sphere of the cations. Further the water molecules in layered double hydroxides also bond to each other, leading to the incorporation of water in excess of what is predicted by the Miyata formula (Miyata, 1975) based on crystal chemical considerations. The excess water is one of the reasons for the poor crystallinity of layered hydroxides.

1 Introduction

The layered double hydroxides (LDHs) are a class of layered materials derived from the structure of mineral brucite, $\text{Mg}(\text{OH})_2$. Brucite comprises infinite sheets of edge shared $[\text{Mg}(\text{OH})_6]$ polyhedra (coordination symmetry, D_{3d}), stacked one above another. The C_3 axes of the coordination polyhedra are parallel to the stacking direction. This yields charge-neutral layers of the composition $[\text{Mg}(\text{OH})_2]$. When the Mg^{2+} ions are partially substituted by trivalent ions such as Al^{3+} , the layers acquire the composition $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}$. Charge neutrality is restored by the intercalation of anions, A^{n-} , in the interlayer region. In addition to the anions, there is a substantial amount of intercalated water owing to the fact that, (i) LDHs are generally obtained from aqueous medium and, (ii) hydroxides have a high affinity for water. Typically, phases with the composition $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2](A^{n-})_{x/n} \cdot y\text{H}_2\text{O}$ ($A = \text{NO}_3^-$, Cl^- , Br^- , CO_3^{2-} , SO_4^{2-} ; $0.2 \leq x \leq 0.33$ and $y = 0.66\text{--}0.8$) are known as Hydrotalcite-like compounds (HTLcs).^[1–3]

LDHs are the exact inverse of cationic clays,^[4] which comprise negatively charged aluminosilicate layers and intercalated cations. The interlayer is richly hydrated and the interlayer water can be reversibly exchanged with the ambient humidity. In general, cations have a high hydration enthalpy and the intercalated water is expected to be associated with the hydration sphere of cations. Recent work by theory and experiment

shows that this is true only when the cations are Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , and Sr^{2+} .^[5,6] In the case of heavier alkali (K^+ , Rb^+ , Cs^+), and alkaline earth metal ions (Ba^{2+}), hydration is essentially of the aluminosilicate layers.

Comparing the behavior of HTLcs with that of the cationic clays, the question arises: Is the intercalated water in LDHs bound to the anions or is it bound to the metal hydroxide layer? The hydration energies of anions are many times smaller than those of cations and it is generally expected that the hydration is more likely of the metal hydroxide layer. However, water molecules can bond strongly with anions through hydrogen bonding – a possibility that is discounted in the context of cationic clays. Indeed, thermogravimetric analysis (TGA) reveals^[7] that LDHs contain water molecules bound with different energies. Some of the water is thought to be adsorbed on the morphological surface as well. There is a general understanding that the adsorbed water is loosely bound in comparison with the intercalated water.^[8] In keeping with this, the $[\text{Mg}\text{--}\text{Al}\text{--}\text{CO}_3]$ LDHs show three mass loss steps in their TGA, attributed to loss of adsorbed water, loss of intercalated water, and decomposition (dehydroxylation and decarbonation) respectively. However in many of the HTLcs, the mass loss steps are not well resolved,^[9] and their sequence is also a matter of debate.^[10,11] In such circumstances, only the total mass loss is measurable with any degree of certainty, and only an approximate value can be assigned to the intercalated water content. The situation is further complicated in some HTLcs, where the intercalated water is exchanged with the vapor phase as a function of the ambient humidity.^[12]

On account of their layered structure, the HTLcs find applications in sorption,^[13,14] ion exchange,^[15–17] drug delivery and environmental amelioration.^[18,19] But the efficacy of the LDH for each of these applications is determined by the layer

* Prof. Dr. P. Vishnu Kamath
Fax: +91-802296-1354
E-Mail: vishnukamath8@hotmail.com (PVK)

[a] Department of Chemistry
Central College, Bangalore University
Bangalore 560 001, India

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201500065> or from the author.

charge, interlayer composition and the degree and strength of hydration. To the extent that these properties remain determined without precision, there are serious limitations to the understanding of the mechanisms underlying these phenomena. In this paper we report the synthesis of a cohort of $[M-M'-A]_x$ LDHs, determine their interlayer compositions and examine the various factors that govern the degree of hydration.

2 Results and Discussion

Single-phase LDH formation was verified by recording the powder X-ray diffraction patterns (PXRD) of the as-precipitated as well as the hydrothermally treated products. The $[Mg-Al-A]$ ($A = CO_3^{2-}$, NO_3^- , Cl^-) samples did not exhibit reflections due to $Mg(OH)_2$ impurity (Supporting Information S1 and S2) over the entire range of nominal compositions $0.15/0.2 \leq x \leq 0.33$. A conclusive way of verifying single phase formation and the degree of isomorphous substitution of Mg^{2+} by Al^{3+} is by measuring the a parameters of the product HTLcs.^[20,21] The a parameter was found to vary linearly with the layer charge, x , in keeping with Vegard's law (Figure 1) in the $[Mg-Al-A]$ ($A = CO_3^{2-}$, NO_3^-) systems. In the $[Mg-Al-Cl]$ system, the a parameter was invariant at $x \leq 0.25$, showing that the LDH formed with only two compositions, $x = 0.25$ and $x = 0.33$.

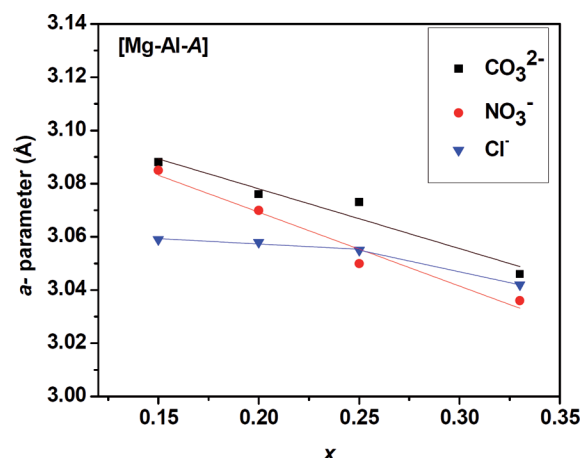
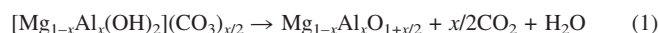


Figure 1. a vs. x plots of $[Mg-Al-A]_x$ ($A = CO_3^{2-}$, NO_3^- , Cl^-) HTLcs.

The anion content of the non-carbonate LDHs was independently determined by ion chromatography as it gives a direct experimental measure of the intercalated anion. In keeping with the conclusions of the PXRD data, the $[NO_3^-]$ content of the $[Mg-Al-NO_3]_x$ system varied in close correlation with the nominal composition (Table 1). In the $[Mg-Al-Cl]$ system, the as-prepared samples were poorly ordered to give any definitive evidence of phase formation. On hydrothermal treatment, they yielded phases, in which $[Cl^-] = 0.26 \pm 0.01$ for all $x \leq 0.25$. In these compositions, the excess Mg^{2+} probably redissolved during hydrothermal treatment. These observations are consistent with the absence of any variation in the a parameter at $x \leq 0.25$.

By taking together, the variation in the a parameter and the anion content, a list of LDHs was compiled and subject to thermogravimetric analysis to estimate y , the total water content (Table 1). Mass loss occurs in numerous steps (Table 2). It is generally observed that a considerable amount of mass is lost starting from just above the ambient temperature up to $100^\circ C$.^[7] To identify the extent of this mass loss, the LDHs were heated to $100^\circ C$ and held isothermally within the TGA system for up to 1 h. From these measurements, the residual water content retained by the LDHs above $100^\circ C$ was estimated as “ z ” (Table 3).

The $[Mg-Al-CO_3]$ LDHs lost between 5 and 15 % of mass below $100^\circ C$ (step I), the proportion increases as the layer charge decreases (Figure 2, Table 2). Above $100^\circ C$, the $[Mg-Al-CO_3]_{0.33}$ LDH exhibits two distinct sigmoidal mass loss steps with inflexions at $225^\circ C$ (step II) and $385^\circ C$ (step III) respectively. The mass loss associated with the step II as well as the temperature of its occurrence steadily decreases with the decrease in layer charge. A mass spectrometric analysis of the evolved gas (Figure 3) clearly shows that both steps I and II are associated with release of water molecules ($m/e = 18$). CO_2 is released only at temperatures in excess of $250^\circ C$ (step III). These results are in agreement with previously published papers.^[11,22–25] The mass loss occurring at step III precisely matches that expected of the decomposition step,^[26]



for all x values, except $x = 0.15$, suggesting that the notional $[Mg-Al-CO_3]_{0.15}$ sample is not a single phase LDH. This composition was deleted from further consideration in this work.

Table 1. Compositions and cell parameters of different LDHs.

System	Anion	Nominal (x)	Cell parameters $a, c / \text{\AA}$	$[A^{n-}]$ by IC	H_2O by TGA (y)
Mg-Al-	CO_3^{2-}	0.33	3.046, 7.63	–	1
		0.25	3.073, 7.90	–	0.81
		0.2	3.076, 7.95	–	0.66
		0.15	3.088, 7.99	–	0.88
	NO_3^-	0.33	3.036, 8.90	0.31	1
		0.25	3.050, 8.76	0.23	0.9
		0.20	3.070, 8.29	0.21	0.9
		0.15	3.085, 8.10	0.15	1
	Cl^-	0.33	3.042, 7.64	0.30	0.53
		0.25	3.055, 7.83	0.25	0.66
		0.2	3.058, 7.89	0.27	0.63
		0.165	3.056, 7.85	0.26	0.90

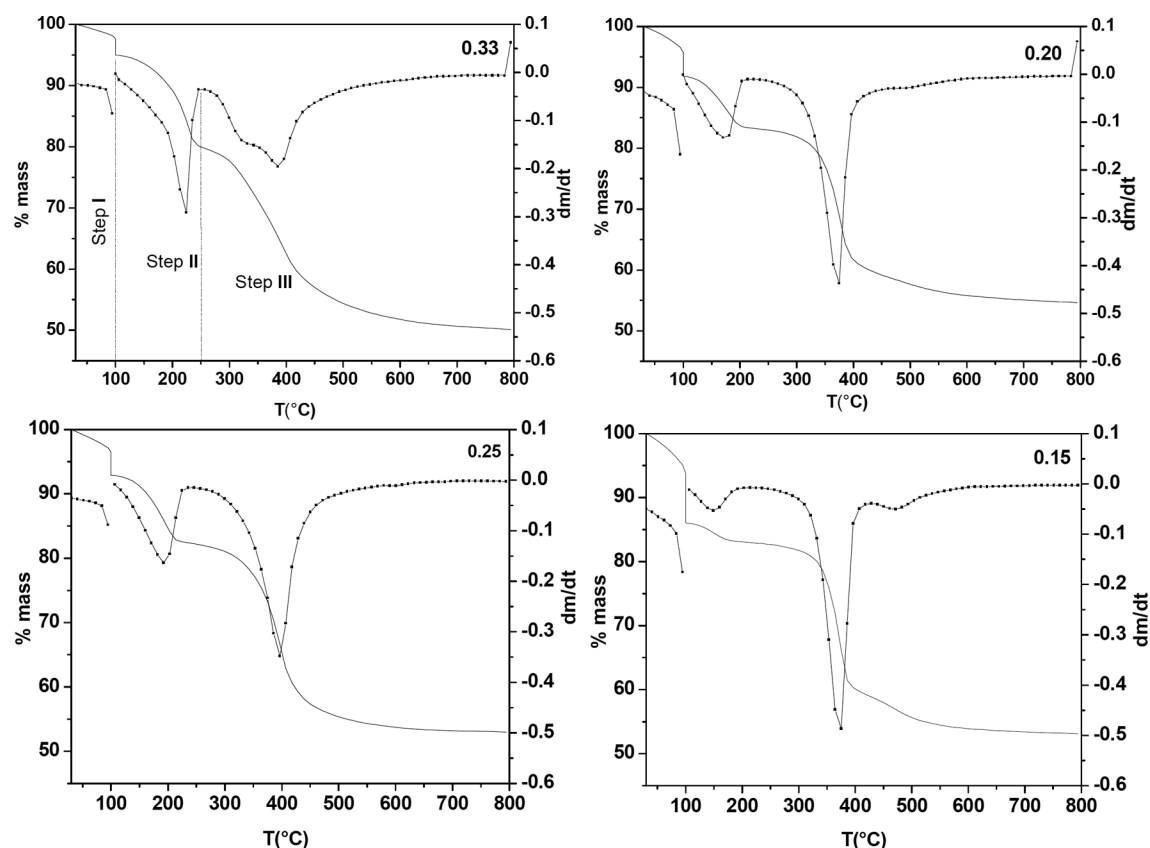
Table 2. Step-wise mass loss suffered by different HTLcs as observed by thermogravimetry.

System		Composition (x)	Step I (30–100 °C) /% mass loss	Step II (100–250 °C) /% mass loss	Step III (250–800 °C) /% mass loss	Total mass loss /%
Mg-Al-	CO ₃ ²⁻	0.33	5	15	30	50.0
		0.25	7.1	10.3	29.6	47.0
		0.2	8.3	8.2	28.9	45.4
		0.15	13.9	3	30	46.9
	NO ₃ ⁻	0.33	10.2	–	45.5	55.7
		0.25	12.5	–	40.1	52.6
		0.2	14.8	–	36.7	51.5
		0.15	14.5	–	34.7	49.2
	Cl ⁻	0.33	9.6	5.4	30.5	45.5
		0.25	9.8	4.6	32.1	46.5
		0.2	9.5	2.9	32.8	45.2
		0.165	11.2	4.3	32.4	47.9

Table 3. The expected and observed water contents of different LDHs and their apportionment between the hydration spheres of the anion and the metal hydroxide layer.

LDH	x	y_{expected}	y_{observed}	y_{excess}	$z^{\text{a)}}$	$(y_{\text{obs}} - z)_{[\text{OH}^-]}^{\text{b)}}$
[Mg-Al- CO_3] $y_{\text{expected}} = 1 - 3x/2$	0.33	0.5	1	0.5	0.75	0.25
	0.25	0.625	0.81	0.18	0.47	0.34
	0.2	0.7	0.66	≈ 0	0.34	0.32
[Mg-Al- NO_3] $y_{\text{expected}} = 1 - 3x$	0.33	0.01	1	0.99	0.47	0.53
	0.25	0.25	0.9	0.65	0.23	0.67
	0.2	0.4	0.9	0.5	0.17	0.73
	0.165	0.5	1	0.5	0.5	0.5
[Mg-Al-Cl] $y_{\text{expected}} = 1 - x$	0.33	0.67	0.53	–	0.1	0.43
	0.25	0.75	0.66	–	0.25	0.41

a) z: degree of hydration of the anion. b) $(y_{\text{obs}} - z)$: degree of hydration of the metal hydroxide layer.

**Figure 2.** The TGA (continuous line) – DTG (dotted line) plots of $[\text{Mg-Al-CO}_3]_x$ ($x = 0.33, 0.25, 0.2, 0.15$) HTLcs. Dotted vertical lines indicates the temperature range of steps I–III.

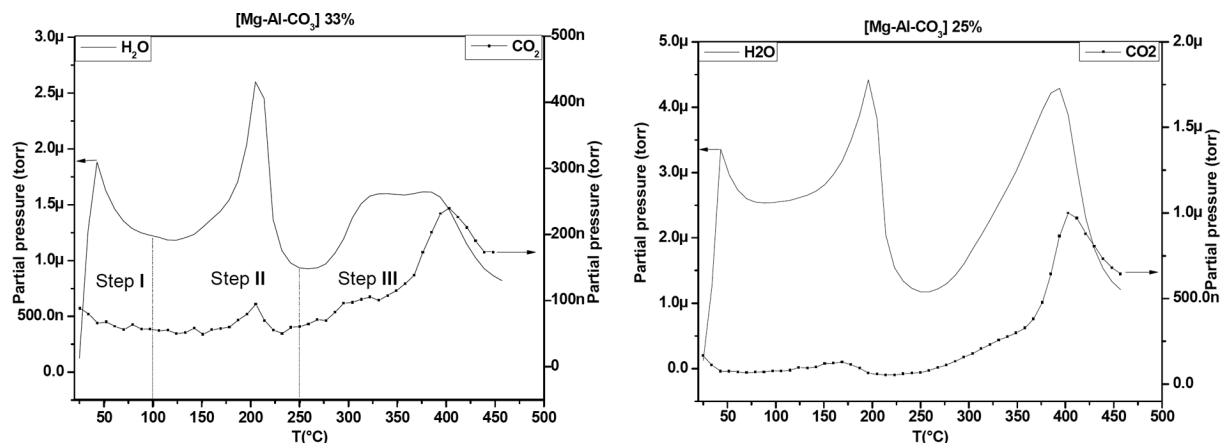


Figure 3. Evolved gas analysis of $[\text{Mg-Al-CO}_3]_x$ ($x = 0.33$ and 0.25) HTLcs. Dotted vertical lines indicate the temperature range of steps I–III.

The water content of the LDHs was then obtained both including (y_{observed}) and excluding the mass loss below 100°C (z) (Table 3). In both cases, the water content scales with the layer charge. This observation raised the question: Is the mass loss below 100°C due to adsorbed water, as is generally believed?

The traditional way of identifying the water species as adsorbed (loss below 100°C) and intercalated (loss between 100 – 250°C) fails in the light of the following observations:

(i) The morphological surface area of LDHs is generally invariant with layer charge.^[27] Thereby the adsorbed water content is also expected to be independent of layer charge – an expectation belied by observations made in this work.

(ii) The LDHs have a very high sorption capacity for anions, which can only be accounted by the behavior of the entire interlayer, lining the galleries, as a single contiguous “structural surface”. Such a behavior erases the difference between adsorbed and intercalated water species.

(iii) There are recent reports of interpolytype transitions in SO_4^{2-} -LDHs accompanied by basal spacing changes brought on by the loss of water molecules below 100°C .^[28,29] The loss of water in vacuo at temperatures below 100°C has resulted in the contraction of basal spacing in $[\text{Mg-Al-NO}_3]$ LDHs.^[30] This shows that the water from within the interlayer is also released below 100°C .

These observations are not consistent with what is expected of adsorbed species.

An alternative interpretation is to assign the water lost below 100°C to that bound to the metal hydroxide layer both within and outside the interlayer gallery. The mass lost between 100 – 250°C is the water bound to the carbonate ions and comprises the hydration sphere of anion. This strongly bound water is released at a higher temperature (step II) than the water bound to metal hydroxide layer (step I).

Henceforth for the purpose of further discussion, the two differently bound water species are described as those bound to the metal hydroxide slabs and those bound to the intercalated anions. As the anion content goes down, the hydration sphere of the anion decreases (step II) with a concomitant increase in the water bound to the metal hydroxide surface (step I).

The variation in the water contents of $[\text{Mg-Al-CO}_3]$ merits a discussion. A majority of the naturally occurring and laboratory synthesized LDHs are known to crystallize in the structure of the $3R_1$ polytype,^[31–33] wherein the stacking sequence of the metal hydroxide layers is AC CB BA AC This stacking sequence offers trigonal prismatic interlayer sites within which the intercalated species are accommodated.

One of the LDHs whose structure is refined with some degree of certainty in this system is the $[\text{Mg-Al-CO}_3]$ LDH.^[31] It is therefore useful to recapitulate the essential feature of this model.

(1) The carbonate ions are intercalated with their molecular plane perpendicular to the stacking direction, also the crystallographic c axis of the LDH crystal.

(2) The structure of the $3R_1$ polytype offers different crystallographic sites in the interlayer: $3b$ - located at the midpoint of the line joining the hydroxyl groups lining the interlayer; $6c$ - located just below the metal site, $18h$ and $18g$ - located at the vertices of hexagons centered around the $3b$ site, the two hexagons rotated by 30° with respect to each other.

(3) The carbon atom is located at the $6c$ site, which is also the centre of the trigonal prismatic interlayer site with the oxygen atoms located at $18h$. The $18h$ site offers the best compromise between hydrogen bonding with hydroxyl groups of the metal hydroxide layers and coulombic bonding which is directed towards the cationic sites.

(4) The oxygen atom of the intercalated water molecule shares the same site as that of the carbonate anion.

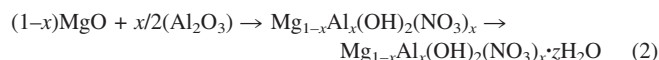
In the event, the oxygen atom of the intercalated water molecule is indistinguishable from that of the carbonate ion. The total oxygen content of the interlayer $3x/2 + y = 1$.^[34,35] An occupancy of 1, also provides for an efficient packing of the interlayer space and enhances the enthalpy contribution to free energy. Here y corresponds to the total water content, which includes the water bound to the metal hydroxide layer (mass loss observed below 100°C , step I) and water bound to the anion (mass loss observed between 100 – 250°C , step II). Based on this formulation, the HTLc with $x = 0.33$ is expected to have $y = 0.5$ yielding the formula $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$. The requirement of maintaining the interlayer oxygen content

at 1, dictates that the water bound to the metal hydroxide slab should increase as x decreases.^[35]

However our analysis shows that the total water content, y , decreases from 1 to 0.66 as x decreases from 0.33 to 0.2 (Table 1) in the [Mg-Al-CO₃] system belying the expectation of Miyata^[35] and Cavani et al.^[1] At the same time, the water content associated with CO₃²⁻ ions (z) also decreases from 0.75 to 0.34 (Table 3). After accounting for the stoichiometric carbonate content, the LDH with $x = 0.33$ composition has excess H₂O to the extent of 0.5 compared to the crystallographically required quantity (see y_{excess} in Table 3). Of this excess nearly half, 0.25 is bound to the carbonate ions and is not lost on staying at 100 °C. The presence of this excess water in the interlayer actually leads to turbostratic disorder that is so widely prevalent in the [Mg-Al] LDH system. The LDH with $x = 0.25$ layer charge has a smaller excess of 0.18, whereas the LDH with $x = 0.2$ has no excess water ($y = 0.66$). This suggests that in the latter, all the crystallographically defined sites in the interlayer are precisely occupied.

In the [Mg-Al-NO₃] system, the LDH with composition $x = 0.33$, lost about 10 % of its mass at 100 °C, whereas the LDHs with lower layer charge lost up to 15 % of their mass at 100 °C. There was no clear separation of the mass losses due to reactions corresponding to steps II and III (Figure 4). In this system, only the total mass loss over the temperature range 100–800 °C was experimentally obtained. Data obtained from mass spectrometric analysis of the evolved gas (Figure 5) was used to divide the total mass lost into the dehydration (step II) and

decomposition (step III) steps. Release of NO was observed only above 350 °C. The partial pressure due to the release of H₂O showed peaks at 125 °C and later again above 400 °C. In the intermediate temperature (240 °C), there was a dip in the partial pressure of H₂O. This minimum was taken to signify the end of step II and the initiation of step III. Assuming the residue to comprise mixed oxides, the LDH can be theoretically reconstructed as,



The value of z was determined as the difference between the mass computed for the anhydrous LDH and the actual observed mass of the LDH after the stay at 100 °C (Table 3). In this case, z corresponds to the extent of water bound to the nitrate ions. The total water content was also computed including the mass loss below 100 °C. The latter yielded a value of $y \approx 1$ for all compositions $0.165 \leq x \leq 0.33$ (Table 3). The water associated with the nitrate ion, z , varied as 0.47 ($x = 0.33$), 0.23 ($x = 0.25$), 0.17 ($x = 0.2$), and 0.47 ($x = 0.165$).

In the [Mg-Al-NO₃] system, the LDH with composition $x = 0.33$ cannot be compared with LDHs of other compositions, as the intercalated nitrate is oriented with its molecular plane inclined at ca. 70° to that of the metal hydroxide layer.^[36] In this orientation, a large amount of water can be included in the interlayer gallery. Nevertheless the oxygen atom of the intercalated water occupies the 18h site. The Miyata formula is not applicable to such a structure where the oxygen atom of the

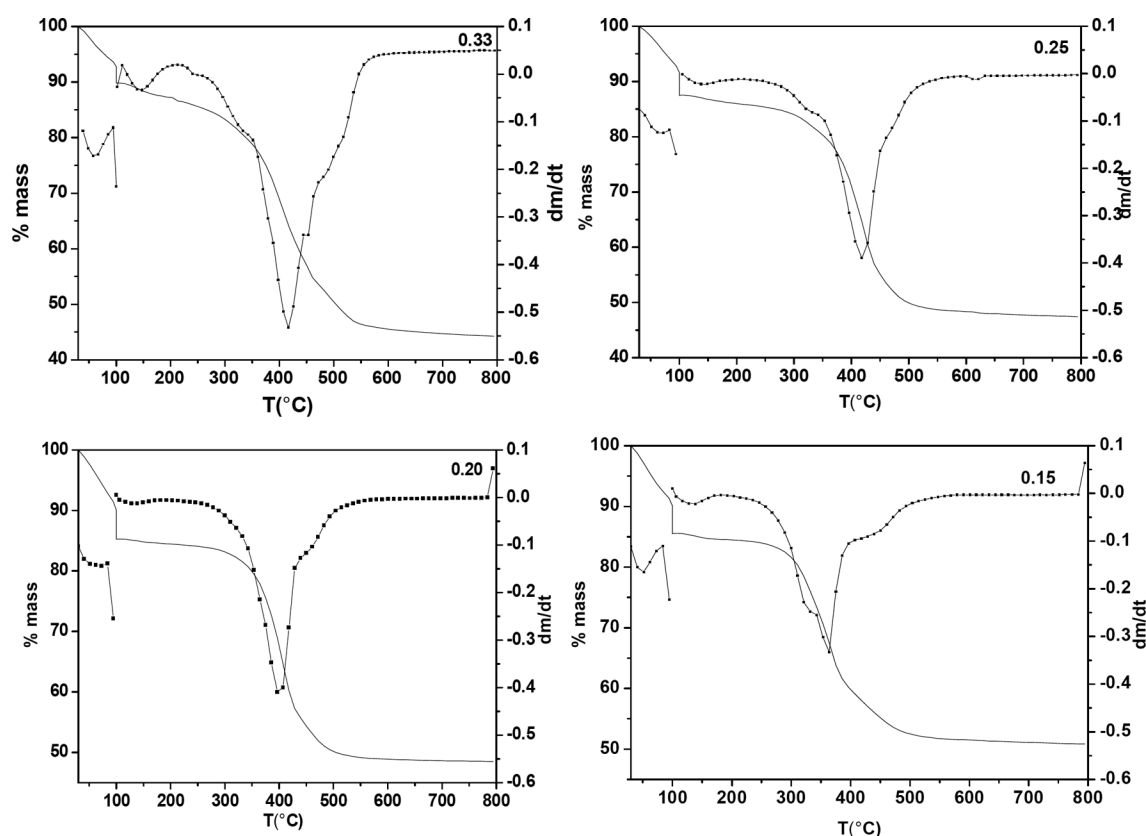


Figure 4. The TGA (continuous line) – DTG (dotted line) plots of [Mg-Al-NO₃]_x ($x = 0.33, 0.25, 0.2, 0.15$) HTLcs.

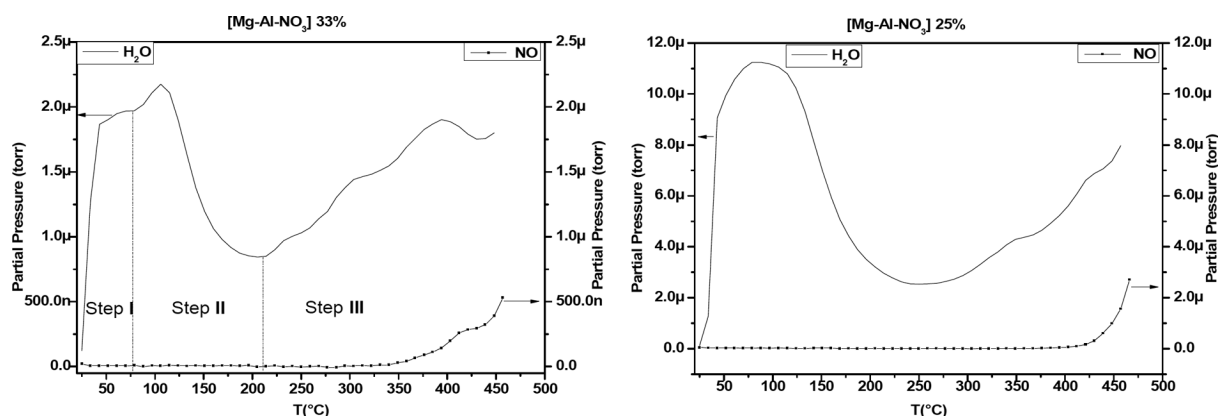


Figure 5. Evolved gas analysis of $[\text{Mg-Al-NO}_3]_x$ LDH ($x = 0.33$ and 0.25). Dotted vertical lines indicate the temperature range of steps I–III.

anion and that of water occupy different crystallographic sites. The observed oxygen content in the interlayer is 2, as opposed to the Miyata formula which limits it to 1. Of this 1 O belongs to the intercalated nitrate ion and the other to the intercalated water molecule. Of the latter, about half (0.47) is retained above 100 °C and is bound to the intercalated nitrate ion. The remaining water, (0.53) is bound to the metal hydroxide layer. At lower layer charge ($x \leq 0.25$), the nitrate is intercalated with its molecular plane parallel to the metal hydroxide layer as in the carbonate-LDH. The lower charge on the nitrate ion indicates that the twice the number of nitrate ions than the carbonates are intercalated for the same layer charge. The Miyata formula stands modified to $3x + y = 1$. The ideal composi-

tion is $x = 0.165$, which compares with the $x = 0.33$ for the carbonate-LDH. The water content expected from Miyata's formula for the $[\text{Mg-Al-NO}_3]$ LDH is 0.25 ($x = 0.25$), 0.4 ($x = 0.2$), and 0.5 ($x = 0.165$) for different compositions. However all these three LDHs have $y \approx 1$, of which 0.23 ($x = 0.25$), 0.17 ($x = 0.2$), and 0.5 ($x = 0.165$) water molecules are retained even after stay at 100 °C and are bound to the nitrate ion [designated as z in Equation (2) above]. The LDHs with $x = 0.25$ and 0.165 satisfy the Miyata formula for their z values (0.23 and 0.50 respectively) rather than the y values. At $x = 0.2$, the water content (0.17) associated with the anion understandably decreases, whereas that associated with the metal hydroxide slab concomitantly increases compared to the LDH with com-

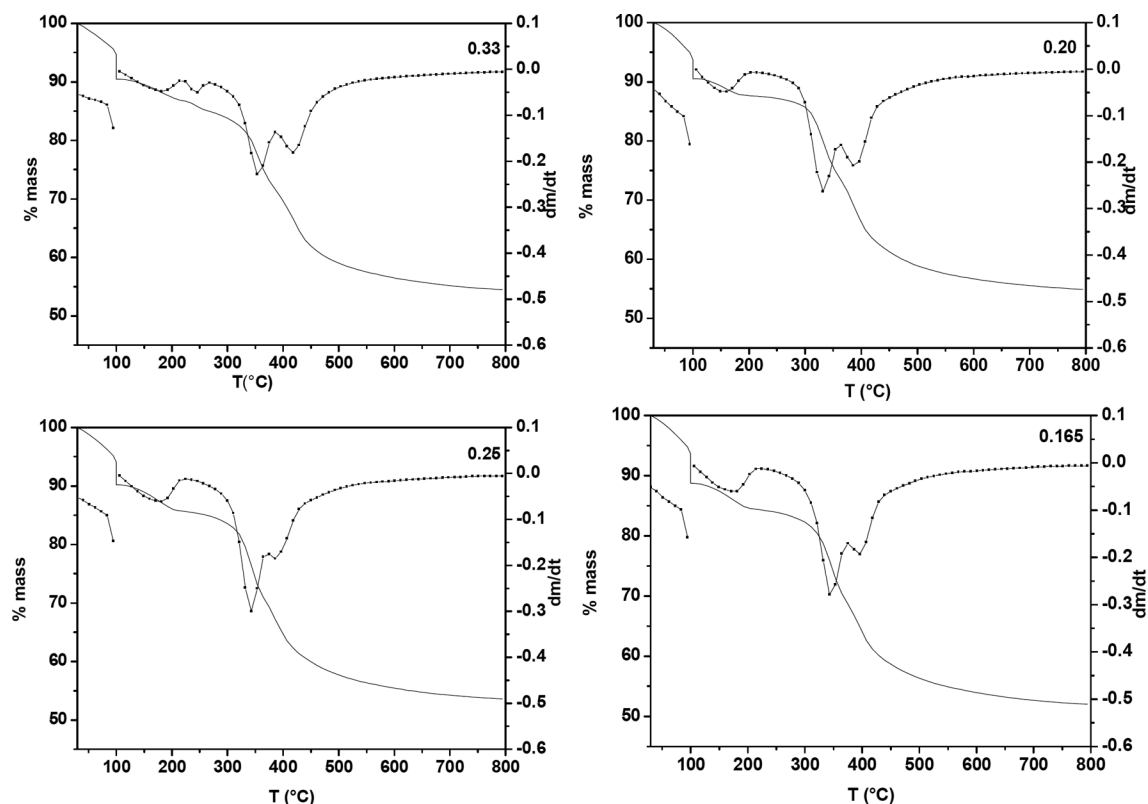


Figure 6. The TGA (continuous line) – DTG (dotted line) plots of $[\text{Mg-Al-Cl}]_x$ ($x = 0.33, 0.25, 0.2, 0.165$) HTlcs.

position, $x = 0.25$. At the ideal composition ($x = 0.165$), the water content is equally distributed between the anion and the metal hydroxide layer. All the three LDHs have water in excess of the crystallographic requirement resulting in structural disorder.

In the [Mg-Al-Cl⁻] system, all LDHs lost ca. 10% of their mass at 100 °C. The LDH with composition $x = 0.33$ showed a single step mass loss in the temperature range 100–800 °C range. However, there are two closely spaced inflection points at 350 °C and 410 °C, respectively (Figure 6). This LDH was analyzed with the same methodology that was used in the case of the nitrate-LDHs. The twin inflection points are seen in all the LDHs in this system. The LDHs with composition $x \leq 0.25$ show a distinct sigmoidal mass loss step below 200 °C. The mass loss steps are very similar and taken together with the fact that the a parameter hardly varies in the range $0.15 \leq x \leq 0.25$, it is evident that all these samples have the same composition. Ion chromatography reveals that the composition is close to $x = 0.25$. Considering all factors, it appears that the [Mg-Al-Cl] system forms only two compositions, one with ca. 0.5H₂O ($x = 0.33$) and the other with 0.66H₂O ($x = 0.25$). After staying at 100 °C, the former is nearly dehydrated, while the latter composition retains 0.25H₂O in the hydration sphere of the chloride ion (Table 3).

3 Conclusions

The water molecules incorporated within the layered double hydroxides are distributed between the hydration spheres of the metal hydroxide layer and the intercalated anion. In carbonate-LDHs the greater proportion of the water is associated with the anion, whereas in the nitrate and chloride containing LDHs, the greater proportion of the intercalated water is bound to the metal hydroxide layer. This trend is in keeping with the higher hydration enthalpy of the divalent anion compared to the monovalent anions.

4 Experimental Section

A wide matrix of synthesis conditions (Table 4) was explored to synthesize a cohort of HTLcs. The [Mg-Al-CO₃] LDHs were prepared by co-precipitation at a constant high pH > 12 following the method of Reichle.^[37] In separate precipitations a mixed metal nitrate solution (total metal concentration 1 M, 20 mL) containing appropriate ratios of the two metals ($x = 0.15$ – 0.33) was added dropwise (drop rate 2 mL·min⁻¹) with constant stirring to a solution of NaOH (1 M, 100 mL, 25 °C) containing five times the stoichiometric requirement of CO₃²⁻ ions taken as Na₂CO₃, with a view to obtain ca. 2 g of the product. The freshly precipitated slurry was stirred for 1 h and kept for ageing (at 65 °C, 12 h) in the oven.

The [Mg-Al-NO₃] LDH was prepared in a similar manner, but by the use of ammonia (1 M, 25–27 °C) as reported elsewhere.^[38] In this case, the composition at the lower range of $x = 0.165$. The use of ammonia prevented the inclusion of CO₃²⁻ ions in the interlayer, while providing a constant moderate pH = 11 throughout the precipitation.

In each case, the product was separated by centrifugation, washed several times and dried at 65 °C in an air oven.

Table 4. A summary of conditions employed for the preparation of LDHs.

System	Anion	Composition (x)	Reference to the synthesis method	T / °C	pH
Mg/Al	CO ₃ ²⁻	0.15–0.33	[37]	room temp.	>12
	NO ₃ ⁻	0.15–0.33	[38]	room temp.	>11
	Cl ⁻	0.15–0.33	pH stat (7) This work	60	8

All the samples were characterized by powder X-ray diffraction (PXRD) with a Bruker D8 Advance Powder diffractometer (source Cu-K α radiation $\lambda = 1.5418$ Å) operating in reflection geometry. Data were collected at 1°2 θ min⁻¹ scan rate. LDH formation is indicated by the presence of 00 l ($l = 1, 2, 3$) basal reflections in the low ($2\theta < 25^\circ$) angle region, and appearance of the 110 and 113 reflections in the high ($59^\circ < 2\theta < 63^\circ$) angle region. The cell parameters are evaluated as $a = 2 \times d_{110}$, $c = l \times d_{00l}$, and errors were evaluated by applying a variation of $\pm 0.1^\circ 2\theta$ in the observed values. In the non-carbonate HTLcs systems, hydrothermally-treated samples were taken for analysis.

The anion content of the non-carbonate HTLcs was determined by ion chromatography using a Metrohm Model 861 Advanced Compact ion chromatograph fitted with a Metrosep SUP5 150 column. A pre-weighed amount of the LDH was dissolved in a mineral acid of a different anion and injected into the chromatograph. The chromatograph response was calibrated using standard stock solutions of the corresponding sodium salts (Aldrich Chemical Co., USA). The carbonate content of the [Mg-Al-CO₃] LDHs could not be estimated by ion chromatography as the moving phase employed is itself a Na₂CO₃ solution.

Thermogravimetric analysis (TGA) was performed with a Mettler Toledo Model 851° TG-sDTA system driven by Star° software. A three segment heating program was employed comprising two ramps (30–100 °C and 100–800 °C, heating rate 5 °C·min⁻¹, flowing nitrogen) with a stay at 100 °C (1 h). The Evolved Gas Analysis (EGA) was done with a Perkin-Elmer TGA connected to the Mass Spectrometry Hiden gas Analyser (25–450 °C, heating rate 5 °C·min⁻¹). The mass spectrum of the evolved gas was recorded at intervals of 50 s. The measurements were carried out in flowing argon.

Supporting Information (see footnote on the first page of this article): PXRD patterns of [Mg-Al-A] ($A = \text{CO}_3^{2-}, \text{NO}_3^-, \text{Cl}^-$) LDHs and a listing of the first basal reflection.

Acknowledgements

The authors thank the Department of Science and Technology (DST), Government of India (GOI) for financial support. P.V.K is a recipient of the Ramanna Fellowship of the DST. The authors thank Dr. G.V. Manohara for EGA measurements and useful discussions.

References

- [1] F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* **1991**, *11*, 173–301.
- [2] V. Rives, *Appl. Clay Sci.* **2001**, *22*, 75–76.
- [3] A. I. Khan, D. O'Hare, *J. Mater. Chem.* **2002**, *12*, 3191–3198.
- [4] T. J. Pinnavaia, *Science* **1983**, *220*, 365–371.

- [5] O. Bildstein, J. M. Douillard, M. Jullien, H. Van Damme, *J. Phys. Chem. C* **2007**, *111*, 13170–13176.
- [6] F. Salles, J. M. Douillard, O. Bildstein, C. Gaudin, B. Prelot, J. Zajac, H. Van Damme, *J. Colloid Interface Sci.* **2013**, *395*, 269–276.
- [7] V. Rives, *Mater. Chem. Phys.* **2002**, *89*, 19–25.
- [8] V. R. L. Constantino, T. J. Pinnavaia, *Inorg. Chem.* **1995**, *34*, 883–892.
- [9] Z. P. Xu, H. C. Zeng, *J. Phys. Chem. B* **2001**, *105*, 1743–1749.
- [10] E. Kanazaki, *Inorg. Chem.* **1998**, *37*, 2588–25908.
- [11] V. Rives, *Inorg. Chem.* **1999**, *38*, 406–407.
- [12] N. Iyi, K. Fujii, K. Okamoto, T. Sasaki, *Appl. Clay Sci.* **2007**, *35*, 218–227.
- [13] J. Das, B. S. Patra, N. Baliarsingh, K. M. Parida, *Appl. Clay Sci.* **2006**, *32*, 252–260.
- [14] R. Chitrakar, S. Tezuka, A. Sonoda, K. Sakane, T. Hirotsu, *Ind. Eng. Chem. Res.* **2008**, *47*, 4905–4908.
- [15] M. Meyn, K. Beneke, G. Lagaly, *Inorg. Chem.* **1990**, *29*, 5201–5207.
- [16] S. Miyata, *Clays Clay Miner.* **1983**, *31*, 305–311.
- [17] M. D. Gillman, G. P. Noble, M. A. Raven, *Appl. Clay Sci.* **2008**, *38*, 179–186.
- [18] R. Rojas, *Applications of Layered Double Hydroxides on Environmental Remediation*, In: *Hydroxides: Synthesis, Types and Applications* (Eds. A. C. Carillo, D. A. Griego), Hauppauge NY: Nova Science Publishers **2012**, pp. 39–71.
- [19] Q. Wang, D. O'Hare, *Chem. Rev.* **2012**, *112*, 4124–4155.
- [20] R. Pausch, I. Lohse, H. H. Schurmann, K. Allmann, *Clays Clay Miner.* **1986**, *34*, 507–510.
- [21] I. G. Richardson, *Acta Crystallogr., Sect. B* **2013**, *69*, 414–417.
- [22] J. Pérez-Ramírez, S. Abelló, N. M. Van Der Pers, *Chem. Eur. J.* **2007**, *13*, 870–878.
- [23] R. L. Klopogge, J. T. Kristof, J. Frost, in *Proc. 12th Int. Clay Conf.*, Bahai-Blanca, Argentina, **2001**.
- [24] T. S. Stanimirova, N. Piperov, N. Petrova, G. Kirov, *Clay Miner.* **2004**, *39*, 177–191.
- [25] F. L. Theiss, G. A. Ayoko, R. L. Frost, *J. Therm. Anal. Calorim.* **2012**, 649–657.
- [26] T. S. Stanimirova, I. Vergilov, G. Kirov, *J. Mater. Sci.* **1999**, *34*, 4153–4161.
- [27] S. V. Prasanna, P. V. Kamath, P. Vishnu Kamath, *Solid State Sci.* **2008**, *10*, 260–266.
- [28] S. Radha, C. A. Antonyraj, P. Vishnu Kamath, S. Kannan, *Z. Anorg. Allg. Chem.* **2010**, 636, 2658–2664.
- [29] R. J. Hou, X. Bish, D. L. Wang, S. L. Johnston, C. T. Kirkpatrick, *Am. Mineral.* **2003**, *88*, 167–179.
- [30] N. Iyi, M. Jobbágy, *J. Phys. Chem. C* **2010**, *114*, 18153–18158.
- [31] M. Bellotto, B. Rebours, O. Clause, J. Lynch, R. M. Cedex, D. Bazin, E. Elkar, *J. Phys. Chem.* **1996**, *100*, 8527–8534.
- [32] I. G. Richardson, *Acta Crystallogr., Sect. B* **2013**, *69*, 150–162.
- [33] S. J. Mills, A. G. Christy, J.-M. R. Génin, T. Kameda, F. Colombo, *Mineral. Magn.* **2012**, *76*, 1289–1336.
- [34] K. Allmann, *Chemia* **1970**, *24*, 99.
- [35] S. Miyata, *Clays Clay Miner.* **1975**, *23*, 369–375.
- [36] S. Marappa, S. Radha, P. V. Kamath, *Eur. J. Inorg. Chem.* **2013**, 2122–2128.
- [37] W. Reichle, *Solid State Ionics* **1986**, *22*, 135–141.
- [38] J. Olanrewaju, B. L. Newalkar, C. Mancino, S. Komarneni, *Mater. Lett.* **2000**, *45*, 307–310.

Received: February 1, 2015

Published Online: March 18, 2015