Layered double hydroxides (LDHs) or the so-called hydrotalcite-like compounds are now widely studied materials due to their potential applications in various research and industrial purposes such as adsorbents, catalysts, catalyst precursors or supports, in medicine, as nanometer-sized composite materials [1-7a]. The extensive application of LDHs is expected by the reason of the anion exchange capacity [5b,8,9] toward inorganic and organic anions [10] and moreover, even layered organic/inorganic hybrid materials could be easily obtained by an ion-exchange reaction of interlayer ions with organic guest anions [11,12].

Structurally, hydrotalcites/LDH can be derived from the brucite structure in which other cations (e.g. Al\(^{3+}\) or Fe\(^{3+}\)) substitute a part of Mg\(^{2+}\) ions. The layers are positively charged due to the isomorphous substitution of bivalent cations by trivalent ones and are intercalated with anions, in order to balance the residual charge. Together with the anions, water molecules are also present in the interlayer domain. The natural occurrence of these materials is rare, but they can be synthesized in the laboratory at relatively low cost [13].

Layered double hydroxides have the general formula \([\text{M}^{2+}\text{M}^{3+}(\text{OH})_2]^{x+}\text{A}^{-}n\text{H}_2\text{O}\), where \(\text{M}^{2+}\) and \(\text{M}^{3+}\) are metal cations and \(\text{A}\) represents the anions to balance the positive charge of the layer. Many research groups have studied LDHs that can be fitted into the above formula by varying the cationic and anionic species [7b,8,14-20]. We present now results concerning some LDH materials with \(\text{M}^{2+} = \text{Zn}^{2+}, \text{Mg}^{2+}\) and \(\text{M}^{3+} = \text{Al}^{3+}, \text{Ga}^{3+}\); \(\text{A}\) is carbonate and/or nitrate. The structure of such LDH samples is composed thus of hydroxide brucite layers and interlayer anions and water as sketched in figure 1.

The samples were prepared in laboratory. Their structure was routinely characterized for structure and texture. Fourier Transform Infrared Spectra (FTIR) and thermogravimetric (TG) measurements were now detailed. The spectra put in evidence the frequencies characteristic for the framework, water and OH groups. Interlayer carbonate and nitrate ions were observed and quantified on the basis of calibration curves.

Experimental part

Synthesis of the Layered Double Hydroxides

The samples containing magnesium and a trivalent metal \(\text{M} = \text{Al}, \text{Ga}\) were synthesized based on a well-established procedure [12,21,22a]. In a typical synthesis, an aqueous solution containing 0.25 moles Na\(_2\)CO\(_3\)\(\times\)10\(\text{H}_2\text{O}\), 0.6 moles Mg(NO\(_3\))\(_2\)\(\times\)6\(\text{H}_2\text{O}\) and 0.1 moles of M(NO\(_3\))\(_3\)\(\times\)x\(\text{H}_2\text{O}\) [23] was brought at alkaline pH (8-10) (with NaOH aqueous solution 50%) then stirred for 2 h at room temperature and for 18 h at 65 °C in sealed bottles. The

![Fig. 1. Lateral view of the interlayer space of the LDH samples](http://www.revistadechimie.ro)

The samples were prepared in laboratory. Their structure was routinely characterized for structure and texture. Fourier Transform Infrared Spectra (FTIR) and thermogravimetric (TG) measurements were now detailed. The spectra put in evidence the frequencies characteristic for the framework, water and OH groups. Interlayer carbonate and nitrate ions were observed and quantified on the basis of calibration curves.
precipitate formed was filtered, washed with bidistillated water (nitrate free) and dried at room temperature overnight. The solids obtained were denoted MgAl and MgGa, respectively. The samples containing zinc as bivalent metal and the Al or Ga as trivalent metal were prepared by the same method, except that the Mg source was replaced with Zn(NO₃)₂ × 6H₂O (0.2 moles). The solids obtained were denoted ZnAl and ZnGa, respectively. The formulae of all the LDH materials were given in table 1 and were based on elemental analysis [12]: the percentages were evaluated assuming only one type of interlayer anion. The percentage of a sample ZnAl when contains only nitrate anions was found similar with that given in the literature [24].

Powder XRD diagrams were collected with an Advance D8 (Bruker) diffractometer with a Cu Kα radiation (λ = 1.5418 Å) operating in theta-two theta geometry. FTIR spectra

Vibrational spectra were recorded between 4000 and 350 cm⁻¹ with a Spectrum BX FTIR spectrometer (Perkin Elmer) by KBr technique, by averaging 128 scans for each spectrum with a resolution of 4 cm⁻¹. Spectroscopic processing such as baseline adjustment, smoothing and analysis was performed using Origin software. Gaussian functions were fitted to the data as previously described [25], getting free all the parameters until squared correlations were higher than 0.995.

Calibration curves were collected using cadmium carbonate (CdCO₃) and sodium nitrate (NaNO₃) of p.a. purity from Merck.

Thermogravimetric analysis

Thermogravimetric measurements were carried out up to 800 °C, simultaneously with differential thermal analysis (DTA) using a Perkin Elmer Diamond apparatus under dry air at a heating rate of 10 K/min. For a limited temperature range, the heating rate was 2 K/min in order to follow the same details of the thermal processes.

Results and discussions

Powder XRD diagrams (as discussed in [12]) have indicated that all the materials have characteristic reflections of the layered structure and high crystallinity; the patterns were indexed in a hexagonal lattice with a rhombohedral space group symmetry. The values of the crystallographic parameters were slightly higher than those expected for a Mg-Al hydrotalcite sample with Mg/Al ratio ~3 and carbonate as charge-balancing anions, because of the presence of nitrate ions in the interlayer space.

In the following we shall focus on the FTIR spectra expecting to observe nitrate ions and on the thermal analysis measurements as well.

FTIR Spectra of LDH samples

A representative spectrum in the region of vibrations of framework and interlayer species is presented in figure 2A for the sample MgGa: the decomposition into Gaussian curves (shown as dotted lines) for the absorption maxima between 1200 and 1800 cm⁻¹ is indicated in the inset as well. The OH stretching vibrations of the same sample are represented in figure 2B, together with their decomposition into Gaussian curves.

For the assignment of absorption maxima we have used a rather rich literature [22b,26-29]. Thus the band at ~1640 cm⁻¹ may be associated with the deformation of water molecule, and the band at 780 cm⁻¹, to the out-of-plane bending deformation of water molecules in the interlayer. The bands below 1000 cm⁻¹ are due to Mg-O/Al-O vibration modes in the brucite layer. The peak at 451 cm⁻¹ is assigned to Mg-O vibration, and the peak at 551 cm⁻¹ is assigned to Al-O vibration.

FTIR spectra displayed also a series of peaks in the region of the framework vibration modes at aprox. 1369, 1390, 1449 and 1463 cm⁻¹; the parameters of Gaussian curves are given in table 2.

The peaks at ~1370 and 1385 cm⁻¹ might be attributed to the carbonate stretching mode: two types of carbonate, namely interlayer carbonate and carbonate associated with metal cations exist in our LDHs. Since the precursors of the LDH materials are nitrates, we expect that the nitrate peaks to appear as well. More about the assignment of anion species vibrations comes from the information on free ion vibration: both carbonate and nitrate free anions have D₃h symmetry and exhibits four normal vibrational modes as shown in table 3. In addition, both anions become
distorted from regular planar symmetry due to environment [30] and the degenerate modes splits into components. Compared to the free carbonate anion, the frequency of the interlayer carbonate is shifted to lower value while by coordination to metal cations it is shifted to higher frequencies. When the carbonate/nitrate ion forms a coordinate bond by means of one (monodentate coordination) or two (bidentate coordination) oxygen atoms and if the planar configuration is maintained, its symmetry decreases from $D_3h$ to $C_2v$ or $C_s$ (table 3). Thus, adsorbed carbonate might be bonded to the surface as uni- or bidentate or as bicarbonate species while adsorbed nitrate ions are bonded via the following adsorption structure: bridging, bidentate and monodentate. However, the interpretations of the infrared spectra are still contradictory. A typical example is the band observed around 1300 cm$^{-1}$, which has been attributed to monodentate nitrate [43], bidentate nitrate [44], solvated nitrate [45], and so on [46]. Whether if adsorbed by one or two oxygen atoms, only two stretching modes are allowed by the surface selection rule (dipole moment parallel to the surface is forbidden). Different models for adsorbed nitrates on Al$_2$O$_3$ were performed [47a] to describe the exact structures of the bridging (1614 cm$^{-1}$), bidentate (1585 cm$^{-1}$) and monodentate (1556 and 1250 cm$^{-1}$) nitrates species, respectively. Noticeably, the band at 1304 cm$^{-1}$ was then assigned to an isolated bidentate nitrate species, involving probably lattice oxygen. In nitrate coordination compounds [48], one-fold coordination gives rise to two symmetric bands (1008 and 1305 cm$^{-1}$) while chelating bidentate nitrate complexes to bands at 1025 and 1476 cm$^{-1}$. The observed shift in band position must be associated with hydrogen bonding to some other unit such as water or the brucite-like hydroxyl surface. Previous studies have suggested that the water in the hydrotalcite interlayer is in a highly ordered structure [47b,c, 49a,b].

The very broad band centered around 3500 cm$^{-1}$ (for the sample MgGa, fig. 2B) is assigned to overlapping stretching modes of hydroxyl groups present, both in the brucite-type layers and in water molecules found between the particles and in interlayers [49c]. Stretching vibrations of OH bonds for water/hydroxyl groups are intense in infrared spectroscopy because of the large change in bond dipole moment. However, the assignment of these bands is difficult because of the initial complex profile of the peak due to the overlap of several bands. The large width of this absorption indicates that there are hydrogen bonded species [50a]. Thus, in the case of Mg$_{6}$Al$_{2}$[OH]$_{16}$[CO$_3$]$_4$H$_2$O, the $\nu_{IR}$ and $\nu_{R}$ are

<table>
<thead>
<tr>
<th>Ion environment</th>
<th>symmetric stretching ($\nu_1$) (IR)**</th>
<th>out-of-plane bend ($\nu_2$) (IR)**</th>
<th>antisymmetric stretch ($\nu_3$) (IR+R)**</th>
<th>bending ($\nu_4$) (IR+R)**</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free $\text{CO}_3^-$</td>
<td>1063</td>
<td>1415</td>
<td></td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>Mg$\text{CO}_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$\text{CO}_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$ calcite</td>
<td>877</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$ aragonite</td>
<td>1083</td>
<td>859</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDH $\text{CO}_3^-$</td>
<td>1000 large</td>
<td>1050 sh#</td>
<td></td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td>Free $\text{HCO}_3^-$</td>
<td>1010</td>
<td>1310</td>
<td>1360</td>
<td>&lt;800</td>
<td>[35]</td>
</tr>
<tr>
<td>Monodentate carbonate</td>
<td>1062</td>
<td>877</td>
<td>1354</td>
<td>1448</td>
<td>[36]</td>
</tr>
<tr>
<td>Bidentate carbonate</td>
<td>1043</td>
<td>865</td>
<td>1282</td>
<td>1590</td>
<td>[36]</td>
</tr>
<tr>
<td>Bridging bidentate carbonate</td>
<td>969-1078</td>
<td>1160-1280</td>
<td>1750-1870</td>
<td>Cited in [37]</td>
<td></td>
</tr>
<tr>
<td>NaAl($\text{CO}_3$)(OH)$_2$</td>
<td>1096</td>
<td>846</td>
<td>1388</td>
<td>1497</td>
<td>[35]</td>
</tr>
<tr>
<td>carbonate-hydroxyapatite</td>
<td>1050</td>
<td>875</td>
<td>1280</td>
<td>1420</td>
<td>[38]</td>
</tr>
<tr>
<td>Free $\text{NO}_3^-$</td>
<td>1050</td>
<td>830</td>
<td>1396</td>
<td>720</td>
<td>[28,30,39]</td>
</tr>
<tr>
<td>$\text{NO}_2$/graphite</td>
<td>1311</td>
<td></td>
<td></td>
<td></td>
<td>[40]</td>
</tr>
<tr>
<td>$\text{NO}_2$/Au</td>
<td>1020</td>
<td></td>
<td></td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>$\text{NO}_3$/hydrotalcite</td>
<td>1019</td>
<td>1062</td>
<td>1157</td>
<td>687</td>
<td>[47]</td>
</tr>
<tr>
<td>NO$_3$/layered double salts</td>
<td>1052</td>
<td></td>
<td></td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>MgAlLDH-nitrate</td>
<td>1053/1042</td>
<td></td>
<td></td>
<td></td>
<td>[41]</td>
</tr>
<tr>
<td>monodentate nitrate</td>
<td>1250</td>
<td></td>
<td></td>
<td></td>
<td>[42]</td>
</tr>
<tr>
<td>bidentate nitrate</td>
<td>1585</td>
<td></td>
<td></td>
<td></td>
<td>[42]</td>
</tr>
</tbody>
</table>

Table 3

Infrared vibration normal modes* of carbonate and nitrate ions

* $R$ means Raman active, IR means IR active. **It becomes IR active when the structure is distorted from regular planar symmetry. ***The degenerate mode is splitted into components in lower symmetry. #Shoulder
five infrared hydroxyl stretching bands are observed at around 2835, 3070, 3354, 3484 and 3602 cm⁻¹. These bands at lower wavenumbers are attributed to strongly hydrogen-bonded water molecules to interlayer carbonate anions.

Table 4 collects the Gaussian parameters of the peaks found in the region of OH stretching.

The presence of bands characteristic of the OH stretching (ν) and bending (δ) of water in the infrared spectrum of the LDHs suggests that these have a certain amount of water entrapped. Presumably, the two hydrogen atoms of such water molecules may hydrogen bond to the oxygen of the network, or to a second water molecule, in either of two distinct ways: in one case, the interaction with the two hydrogen atoms of water is symmetric (type I); in the other, the hydrogen bonds are of different lengths, and probably of unequal strengths as well (type II). In pure liquid water itself, [51] has been provided spectroscopic evidence that symmetrically bound molecules of type I exhibit a pair of OH frequencies, corresponding to out-of-phase and in-phase OH stretching modes, at ~3440 (strong) and 3240 cm⁻¹ (weak), respectively. For the asymmetrically hydrogen-bonded species of type II, the stretching frequency of the longer OH moiety with the weaker hydrogen bond is about 3625 cm⁻¹ (weak), while that of the shorter and more strongly hydrogen-bonded OH is near 3410 cm⁻¹ (strong).

Two of the observed OH stretching infrared bands in the room temperature spectrum of water lodged in the LDHs appear at values remarkably similar to those calculated for the asymmetrically hydrogen-bound molecules in liquid water [51]. The band at 3220 cm⁻¹ is probably associated with the overtone of the deformation at 1632 cm⁻¹ plus the symmetric OH stretching vibration of some symmetrically bound water. The relative intensities of these three bands suggest that the majority of the water held within the cavities of the LDHs is asymmetrically hydrogen-bonded.

The bands at high wavenumbers (~3800 cm⁻¹) would prove the existence of OH groups coordinated to metal ions; those at 3650-3550 cm⁻¹, might belong to bridged OH groups interacting with adsorbates as in zeolites [52-54] while those at 3668, 3331 and ~3250 cm⁻¹ might be due to water in a highly structured environment between the hydrotalcite layers. These later bands are attributed to water coordinated to the M-OH units, and the bands at 3434 and 3400 cm⁻¹ to water molecules found between the hydrotalcite layers. In other studies [50b,c], these bands have been attributed to Al-OH stretching vibrations. Anyhow, the position of the bands implies that the water in the hydrotalcite layers is highly structured.

Thermal analysis

Representative TG curves with the corresponding DTG derivatives are illustrated in figure 3. Two apparent endothermic events at 180 and 450 °C with a high broad endothermic peak at about 360°C. The first one can be assigned to the loss of interlayer water, and the second and minor ones can be assigned to the loss of hydroxyl ions and removal of carbonate ions, [55] though the temperature is slightly lower than the reported values [26b]. This is in agreement with Miyata[15b] who assigned the 430 and 480 °C to the loss of OH- and Cl-, respectively in LDH materials with Mg, Al and Cl.

The thermogravimetric parameters for the LDH samples studied are summarized in Table 5. The total weight loss after calcination at ca. 800 °C of sample MgAl amounts to ca. 44.6 % of the initial sample weight, of which dehydration accounts for 13.6%, whereas dehydroxylation and combustion of the interlayer anion contribute around 21 %.

Non-freezable water is generally found for molecular sieves [56]. The LDH samples undergo a progressive weight loss in several steps when the temperature increases. The ill-defined inflection points that can hardly

---

**Table 4**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position (cm⁻¹)/Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl</td>
<td>3585/26 3656/76 3499/70</td>
</tr>
<tr>
<td>ZnAl</td>
<td>3585/44 3650/10.5 3586/49 3434/95</td>
</tr>
<tr>
<td>ZnGa</td>
<td>3587/13 3522/16 3432/217</td>
</tr>
</tbody>
</table>

**Table 5**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss (°C)</th>
<th>Temperature at DTG peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAl</td>
<td>31.2</td>
<td>182</td>
</tr>
<tr>
<td>ZnGa</td>
<td>23.4</td>
<td>177</td>
</tr>
<tr>
<td>MgAl</td>
<td>44.9</td>
<td>195</td>
</tr>
<tr>
<td>MgGa</td>
<td>39.4</td>
<td>191</td>
</tr>
</tbody>
</table>

* weight of the anion lost. ** b-broad. *** sh-shoulder
be distinguished in the TG curves were better defined when comparing with the associated DTG and DTA curves (not shown).

The peaks corresponding to decarbonation are at ~433 and 530°C as expected. Water physisorbed on the surface desorbs at temperatures less than 120 °C while the peak at ~250°C shows the dehydroxylation of the water positioned in the interlayer spaces [57,58] then the dehydroxylation process starts leading to an endothermic effect, extended up to ca. 320°C. These processes lead to the collapse of the layered structure. A further step or possibly even more steps are related to the transformation and/or removal of the interlayer anion [58a]. More information comes from modeling the hydration of hydrotalcites [58c]. It was shown that the Al-polyhedra in the hydroxide layers are quite regular; instead, the Mg-polyhedra are distorted ones. In addition most of the Mg cations have either a water molecule or an interlayer anion coordinated thus forming a 7-coordinate site. The displacement of Mg atoms from the middle of the hydroxide layers results in the formation of a much less regular network of hydrogen atoms. Generally, for the carbonate-LDH, the weight loss at below 280°C is attributed to the desorption of water intercalated in the LDH galleries and of adsorbed extracrystalline water on LDH sheets [59]; the weight loss above 450°C corresponded to the CO₂ evolution of the carbonate-LDH [60].

The values of weight loss between 200 and 400 °C (Table 5) do not coincide perfectly with the nitrate amounts expected as shown in table 1, which also shows that some carbonate still exist in the obtained materials.

Quantitative analysis of the spectra

It was difficult to perform a direct quantitative comparison of our sample as concerning the carbonate amount by looking only at the decomposed spectra even though they come from the same sample amount. However, the rather narrow peaks in the region 1350-1450 cm⁻¹ indicate the majority of two nitrate species and one or two carbonate ones. The sample sequence from the point of view of the nitrate presence seems to be at first sight: MgAl ~ ZnAl > MgGa while the carbonate species might be in the order ZnGa > MgGa ~ ZnAl (the species responsible for the absorption around 1510 cm⁻¹) and MgAl > ZnAl > MgGa > ZnGa (the species responsible for the absorption around 1410 cm⁻¹). For this quick evaluation, it was not possible to consider the area of the characteristic peaks taken up to a base line given by the absorption in the range 620-670 cm⁻¹ [26b], which was assigned to the vibrational modes of the hydroxide octahedral layers of the hydrotalcite because of some supplementary absorptions.

However, a more quantitative estimation requires calibration curves. We failed to find credible values of the nitrate amount based on the extinction coefficients given for nitrate impurity species in single crystals [61]. Therefore for a more correct quantitative analysis of our LDH samples, calibration curves were drawn. Some salts with the corresponding anion, cadmium carbonate and sodium nitrate which are not hydrated and either amorphous or with almost reassuring polymorphism of rather high transition temperature were chosen. KBr pellet method gives a good accuracy because each time the same instrument and consistency in sample preparation (the same weight of sample was placed in the same weight of the pellet) were kept to reduce variations in the spectra. The temperature at which these spectra were collected was reasonably constant as well.

The spectra leading to calibration curves for the nitrate and carbonate ions are given in figure 4. These spectra show additionally the presence of some impurity ions, such as sulfates and nitrates, in carbonate and sulfates and phosphates in nitrate. However, the peaks corresponding to these impurities are very small and sharp and do not disturb the spectra used to determine the calibration curves. For carbonate calibration curve we can chose the out-of-plane bending vibration (v2) giving a very sharp peak at 853 cm⁻¹ [62] while for nitrate, that at 836 cm⁻¹. The calibration curves obtained by considering these peaks are presented in figure 5A,B. The band at 1400 cm⁻¹, attributed to an antisymmetric vibration of the CO₃ (or NO₃) stretch, is very wide and can be resolved into components (e.g. into two bands at 1365 and 1410 cm⁻¹) [63]. However, these are peaks of highest intensity and were then further considered for analysis (fig. 5A',B').

Using these calibration curves, the sample composition was estimated and the obtained values are given in table 6.

It results that the investigated LDHs have nitrate ions, whose amount varies in order: ZnAl ~ MgGa > MgAl > ZnGa

![Fig. 4. Spectra providing calibration curves for (A) nitrate and (B) carbonate ions at increasing concentrations of the corresponding salts (in the range 1.2 to 5 mg). The spectra were displaced on the vertical scale for clarity reasons.](http://www.revistadechimie.ro)
where ZnGa has the lowest nitrate amount (at the observability limit). At the same time, the expected sequence from the elemental analysis would be

\[
\text{ZnGa > MgGa > MgAl}
\]

The TG behavior of the sample ZnGa which is not sustained by the infrared measurements might be explained by the Zn excess found by elemental analysis. Another exception is given by the sample ZnAl, which has an excess as well (of Al, this time) and the amount calculated is higher than that found by TG measurements. The agreement is rather good for two of the samples, and under limits usual in the literature [64].

Conclusions

For the samples which do not have excess of network cations, the determination of nitrate/carbonate by thermal analysis measurements corroborated well with FTIR spectroscopy: might constitute a laboratory method for characterization of catalysts resulting from LDH.

Acknowledgements: The financial support by Romanian Ministry of Education and Research (CORE Program, Project PN09-45) is gratefully acknowledged.

References
