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Research Article

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Intercalation and Complexation of Co(II) and Ni(II) by Chelating Ligands Incorporated in Zn-Al Layered Double Hydroxides

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Abstract: Zn,Al layered double hydroxides (LDHs) intercalated by a series of organic chelating ligands (L), including anionic ethylenediamine-N,N-diacetate (EDDA), nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), and diethylenetriaminepentaacetate (DTPA) as guests, were prepared by co-precipitation and anion exchange of precursor Zn,Al-NO_3 LDHs. The chelation of transition metal ions (Co^{2+} and Ni^{2+}) from aqueous solution and the intercalation of pre-formed complexes of the type $[M(edda)]^{2-}$, $[M(nta)]^{-}$, $[M(edta)]^{2-}$ and $[M(dtpa)]^{3-}$, have been investigated. Powder X-ray diffraction (PXRD) showed that the basal spacing increased from 9.0 Å for the precursor materials to 12.0-15.3 Å for the pillared hybrids. Elemental analysis and FT-IR spectroscopy indicated that most of the interlayer nitrate anions were displaced by L anions to form LDHs-L, which then reacted with the metal ions to form $[M(L)]^{n-}$ complexes between the LDHs layers. The compounds were studied by thermal gravimetric (TG) and differential thermal analysis (DTA).

Keywords: Layered double hydroxides; Intercalation; Metal ions; Chelating ligand.

1. INTRODUCTION

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds, represent an important class of materials. Interests in these layered structures have increased because of their potential application as nanocomposite and porous materials formed by intercalation of polyoxometallates and a variety of other molecules which can serve as adsorbents, molecular sieves and catalysts for various chemical reactions [1, 2]. The general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\cdot zH_2O$, where M^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}, etc., M^{3+} = Al^{3+}, Cr^{3+}, Ga^{3+} etc., and x is the ratio $M^{2+}/(M^{2+}+M^{3+})$, presents a structure involving positively charged mixed metal hydroxide layers separated by charge-balancing anions (A^{n-}) and water molecules [3-6]. The anions are exchangeable, giving rise to rich intercalation chemistry. The use of these

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layered inorganic solids as frameworks for the creation of inorganic–organic host–guest supramolecular structures is of increasing interest. Hence, a large number of organic and inorganic anions have been incorporated into LDHs using different methods [7-10]. A particular class of LDHs is one in which the interlayer anion is an organic molecule. Organic intercalates in inorganic host structures of LDHs are considered as one class of hybrid compounds. Under top tactic ion substitution, the organic guest is introduced in the inorganic host matrix with the retention of the overall structure [11]. From a structural point of view, layered hybrid materials combine all the benefits of both the layered host with its expansion and surface properties and interstratified 2D organic domain with its ability to adsorb organic materials. As much as LDHs play an important role in ion exchange and adsorption of organic molecules, it is rather possible that LDH materials can be used as potential matrixes in modelling controlled-release drug formulations through the intercalation of drug molecules [12]. The organo-LDHs properties, characterization and applications have been reviewed recently [13]. The usual preparation method of the organo-LDHs is the direct method in which the organic anion is co-precipitated with the M^{2+}- M^{3+} solution mixture. The second method is by conventional anion exchange. The third less common method is based on the reconstruction property of the calcinated LDHs host. After calcinating the LDHs at temperatures above 450 ^{o}C, mixed metal oxides will be formed. It absorbs anions from solution during the reconstruction of the original structure [14].

Recently, attention has been given to LDHs which contain organic chelating ligands in the interlayer space such as EDTA (ethylenediaminetetraacetate) and NTA (nitrotriacetate) for the use in various chemical reactions and for extraction, preconcentration of metal ions from environmental samples [15]. In addition, the LDHs host serves as sorbent for many organic contaminant anions present in natural waters such as pesticides, phenols, carboxylates, sulfonates and of course various heavy metal ions [16-20]. Investigations on the intercalation compounds of transition metal complexes have shown that guest-host interactions can affect the geometric, chemical and electronic properties and stability of intercalated complexes [21]. Cu(II) and Ni(II) – NTA ($[Cu(nta)]^{-}$ and $[Ni(nta)]^{-}$) complexes have been intercalated into [Zn-Cr] LDHs by direct and indirect anion exchange methods [22]. More recent advances are the in-situ polymerization and intercalation of polymers into layered double hydroxides and their kinetic studies using in-situ x-ray powder diffraction [23, 24].

In the present work, the intercalation characteristics of organic chelating ligand anions with different number of carboxylic groups of two for (edda) , three for (nta), four for (edta), and five for (dtpa) into Zn-Al layered double hydroxides were evaluated under different synthetic conditions and by two methods of direct co-precipitation and anion-exchange. In addition, we have studied the complexation ability of the Zn-Al LDHs pre-intercalated with different ligands (L) to Co(II) and Ni(II) ions from aqueous solutions to form $[M(L)]^{n-}$ complexes. The direct intercalation of $[Co(L)]^{n-}$ and $[Ni(L)]^{n-}$ complexes to Zn-Al-NO_3 precursor by ion-exchange have also been examined. The intercalated structure of Zn-Al-L and $[M(L)]^{n-}$ complexes intercalated LDHs have been examined by powder XRD, FT-IR, EA, and TG-DTA techniques.

2. EXPERIMENTAL

2.1. Materials and Instrumentation

The starting materials $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, 50 % aqueous NaOH, and aqueous solutions of EDDA, NTA, EDTA, H_4Y or H_nY (where $H_nY^{(4-n)-}$ is one of the four possible anions of EDTA depending on the pH), and DTPA were obtained from commercial sources and used as received.

Elemental microanalyses for CHN were performed on Euro EA 3000 elemental analyzer. Powder X-ray diffraction (PXRD) data were collected at room temperature on a Philips X'pert 3065 diffractometer with a curved graphite monochromator (Cu K_α radiation), in a Bragg–Brentano para-focusing optics

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configuration. Samples were step-scanned in 0.02° 2θ steps with a counting time of 1 s per step. FTIR spectra were obtained with KBr pellets using a Mattson Infinity FTIR 60 AR infrared spectrophotometer. All these analyses were carried out at the Institute for Inorganic Chemistry, Friedrich-Alexander University, Erlangen-Nürnberg, Germany.

2.2. Synthesis of Zn_2/Al-NO_3

The initial LDHs, [Zn_2/Al-NO_3], used in anion-exchange reactions, was synthesized according to established methodologies. 18.8 g of $Zn(NO_3)_2.6H_2O$ and 11.7 g of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 80 mL of deionised decarbonated (DD) water to give a total metal Zn: Al ratio of 2 . This solution was then added dropwise to another solution consisting of 6.25 g NaOH and 9.1 g $NaNO_3$ in 44 mL DD water. The mixture was stirred during the precipitation reaction at 60 ^oC for 1 h. The pH was maintained at 8-9 using a NaOH solution. The resulting gel-like slurry was aged at 70 ^oC for 24 h. This slurry was filtered and washed with hot DD water followed by a small amount of acetone to facilitate drying, and kept to dry in air for 12 h at 65 °C.

2.3. Intercalation reactions

*2.3.1. Synthesis of [Zn_2/Al–L] Coprecipitation (CP***)**

The L-intercalated LDHs were prepared by the CP method following closely a reported procedure [25]. Typically, solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.97 g) and $Al(NO_3)_3 \cdot 9H_2O$ (1.12 g) in DD water (100 mL) was prepared. Another aqueous solution of L (0.1 M), (L= ethylenediamine-N,N-diacetate, nitrilotriacetate, ethylenediaminetetraaetate, and diethylenetriaminepentaacetate) was prepared with NaOH (0.5 g) in (50 mL). The NaOH solution was added beforehand to dissolve the acidic form of L and to adjust the solution to pH ~7. This solution was added dropwise, with good stirring, to 150 mL of the metal solution, maintaining the pH in the range 8–10. The resulting gel-like slurry was aged overnight at 70^oC, filtered and washed several times with DD water and dried in air at 65 ^oC for 12 h.

2.3.2. Synthesis of [Zn_2/Al–L] Anion exchange (EX)

In this case, 6 g of the [Zn_2/Al-NO_3] precursor were suspended in 0.5 L of 0.01 M aqueous solution of ligand L of interest. The ligand solution was prepared by mixing solutions of L and NaOH, with acid/base ratio varying from 1:2 to 1:5 to give pH ~7. The suspension was kept on a slow stirring for 12 h at 60 ^oC. The product was filtered and air dried at room temperature. FT-IR spectroscopy was used to check the completeness of anion exchange.

2.3.3. Synthesis of Zn_2/ Al–[M(L)]$^{n-}$

An aqueous suspension of Zn_2/Al-NO_3 was added to a solution of metal complex of the type Na_m[ML], M= Co^{2+} or Ni^{2+} (ca. 50 % in excess was added to ensure complete exchange of nitrate anions) in DD water (70 mL) at room temperature, and the mixture stirred slowly overnight at 60 °C. The solid product was isolated by filtration, washed several times with DD water and dried in air at 65 °C. The metal- L complexes were prepared according to the method described in the literature [15]. The appropriate 0.1 M metal nitrate solution was added to a 0.1 M solution of organic ligand salt (L) and heated at 100 ^oC for 2 h. The solution mixture was filtered to remove the excessive solids and crystallized by evaporating the solution to one-third of the initial volume, followed by cooling in an ice bath. Addition of diethyl ether gave rise to precipitation of the desired complex salt.

2.3.4 Co^{2+} and Ni^{2+} intercalation in [Zn_2/Al–L]

2 g of [Zn_2/Al–L] prepared by the CP method, were suspended in 50 mL of either a Co^{2+} or Ni^{2+} nitrate salt solution. The concentration of the solutions was varied between 0.01-0.05 M. The suspensions were kept at room temperature with occasional shaking for 24 h. The solid was then filtered, washed with DD water and dried in air at room temperature. An immediate observation of the metal sorption was evident by the colouration of the solid Zn_2/Al–L host.

Anal. Calcd for Zn_2/Al–Co(edta) : $Zn_2Al(OH)_6[CoC_{10}H_{12}N_2O_8)]_{0.85}$. H, 3.39; N, 2.40; C, 10.36; H_2O

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12.5%; Found: H, 3.41; N, 2.41; C, 10.39; xH_2O 12.5%.
Anal. Calcd for Zn_2/Al–Ni(edta): $Zn_2Al(OH)_6[NiC_{10}H_{12}N_2O_8)]_{0.85}$. H, 3.39; N, 2.40; C, 10.36; H_2O 12.5%; Found: H, 3.40; N, 2.40; C, 10.38; xH_2O 12.5%.

The xH_2O represent the number of water molecules per mol of Zn_2/Al -L compound which can be calculated for each compound using the equation: 18x = w(m + 18x) / 100. Where, x is the number of H_2O molecules, w is the % weight loss of water(taken from TG analysis) and m is the molecular weight of anhydrous compound.

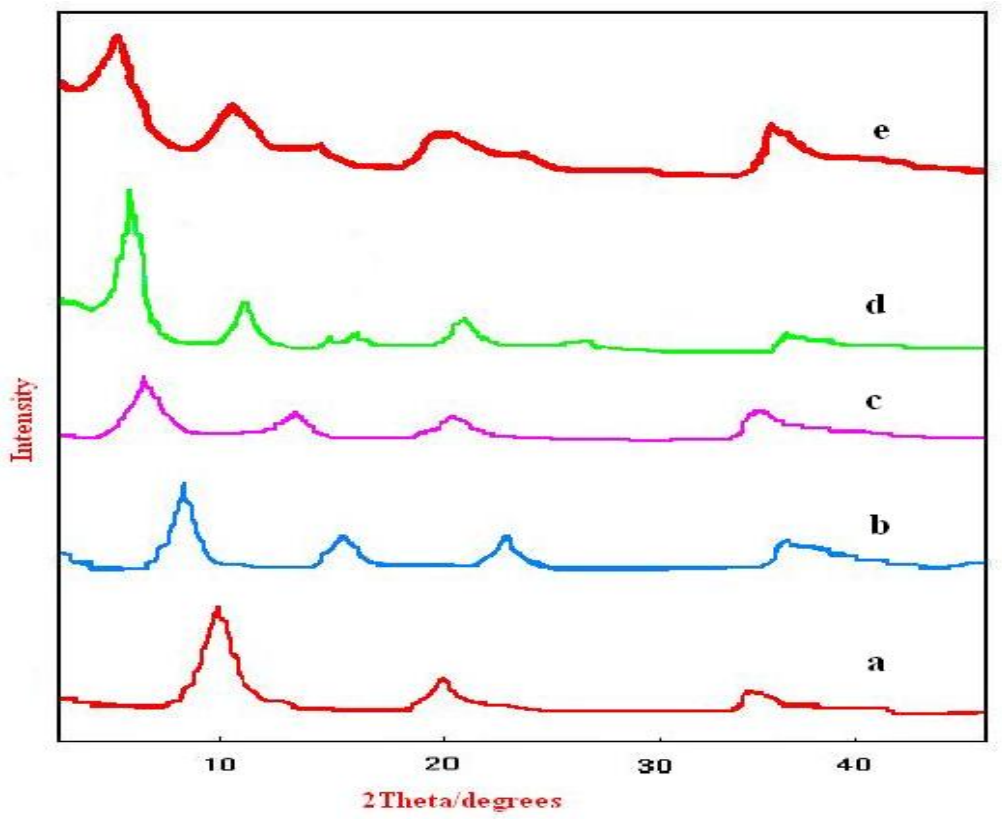

Figure 1. XRD patterns of (a) Zn_2Al-NO_3; (b) Zn_2Al-edda^{-2} ; (c) Zn_2Al-nta^{-3}; (d) Zn_2Al-edta^{-4}; (e) Zn_2Al-dtpa^{-5}.

3. RESULTS AND DISCUSSION

The synthesis of [Zn_2/Al–L] intercalate by CP or EX methods showed that the conditions of the precipitation reaction have a great influence on the precipitate. Simply mixing the solutions will not result in any precipitates as the pH of 4.5 might not be appropriate for the LDHs formation, another aluminium (oxy)hydroxide phase might be expected to precipitate. Increasing the pH to ca. 8.5 and maintaining the Zn: Al ratio of ~ 2, gave the best sample of the EDTA intercalate. Above pH 10, LDHs still precipitates but particle size and yield were reduced noticeably. Table 1, summarizes the data from the PXRD measurements for all of the intercalated materials. These data indicate the similarity for the samples prepared by anion exchange and coprecipitate methods. For NTA as an example, the PXRD patterns indicate a basal spacing of approximately 12 Å, for the two samples prepared by CP and EX methods, respectively. With a better resolved spectra and more sharp (003) diffraction peak for the CP sample, which is usually unexpected. Fig. 1 shows the spectra for precursor material and all the intercalated ligands by co-precipitation method only. However, anion exchange remains easy way to intercalate these

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ligands specially NTA from the view point of the affinity of this anion to the LDHs is stronger than that of NO_3^- anion [26]. The EX method is also common for preparation of organo-LDHs in general, since the properties of the layered material that contain simple inorganic anions allows an easy exchange with mono and divalent anions. This method is well documented in literature [27, 28]. It has been found that LDHs with nitrate anions are the most suitable precursors for such type of exchange [29].

The powder XRD patterns of $Zn_2Al\text{-}NO_3$ is typical of a layered material, similar to those reported in literature [30], except for the (006) peaks which are shifted to lower 2θ values. All (003) reflections are observed up to 5.7° 2θ. The basal spacing d_{003} shifted from about 9.01 Å for $Zn_2Al\text{-}NO_3$ to 15.31 Å for the pillared LDHs. Assuming a thickness of ca. 6.3 Å for the Zn(II)–Al(III) double hydroxide layer, these results indicate that the gallery height generated in the hybrid materials is 10.51 Å. The powder PXRD pattern for the precursor material LDHs contains sharp reflections above ca. 2θ = 30°, indicating larger crystallite sizes, and better defined reflections, indicating a good order in the layer stacking. The lattice parameter *a*, which corresponds to the average metal–metal distance in the layers, was calculated as $2d_{110}$ = 3.06 Å for all samples. As expected, this did not change after intercalation of the metal-ligand complex.

Table 1. PXRD data, method of preparation and pH.

Prepared Compounds	Method of Preparation	pH	d (*003*), Å	d (*006*), Å
$Zn_2Al\text{-}NO_3$	-	8-9	09.01	4.46
$Zn_2Al\text{-}edda^{-2}$	(CP)	10	11.20	7.21
$Zn_2Al\text{-}edda^{-2}$	(EX)	7.0	11.02	-
$Zn_2Al\text{-}nta^{-3}$	(CP)	10	12.04	7.51
$Zn_2Al\text{-}nta^{-3}$	(EX)	7.5	12.01	6.95
$Zn_2Al\text{-}edta^{-4}$	(CP)	8.5	14.38	7.20
$Zn_2Al\text{-}edta^{-4}$	(EX)	7.5	14.13	7.11
$Zn_2Al\text{-}dtpa^{-5}$	(CP)	9.5	15.31	7.36
$Zn_2Al\text{-}dtpa^{-5}$	(EX)	6.5	15.21	7.30

Table 2. Selected Intercalated compounds with Ni(II) and Co(II) complexes.

Prepared Compounds	pH	d (*003*), Å	d (*006*), Å
$Zn_2Al\text{-}(Ni\text{-}nta)^-$	4.5	11.82	6.23
$Zn_2Al\text{-}(Co\text{-}nta)^-$	6.5	11.95	7.02
$Zn_2Al\text{-}(Ni\text{-}edta)^{-2}$	5.2	14.06	7.13
$Zn_2Al\text{-}(Co\text{-}edta)^{-2}$	6.2	14.13	6.98

In Table 1 the basal reflections are displayed, from which the interlayer spacing of the LDH may be deduced. The maximum height 15.31 Å phase is present for $Zn_2Al\text{-}dtpa^{5-}$ (CP), although the basal reflections become weaker and shift slightly to higher angles by changing the method of preparation to ion exchange (EX). There is no indication for a significant re-orientation of the guest molecules upon complexation, as observed; only a slight decrease in the basal spacing at a higher angle is observed for all samples.

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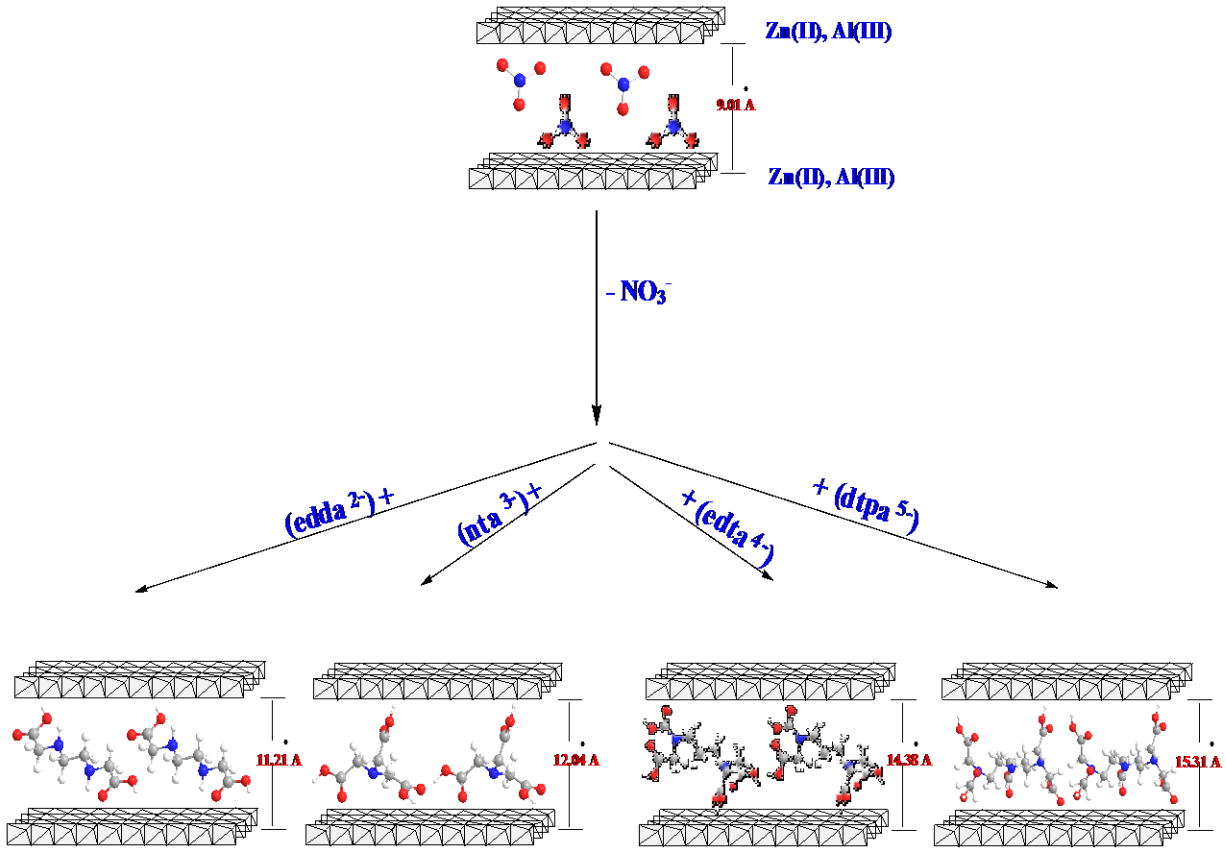

Scheme 1. Presentation of the intercalation reaction of: edda^{-2} , nta^{-3} , edta^{-4} and dtpa^{-5} ligands into the host layers of Zn_2Al-NO_3.

The compact arrangement, scheme 1, however, is proposed due to the strongly separated hydroxyl layers and weak bonging interactions between intercalated species and hydroxyl layers [22]. Furthermore, the decrease of basal spacing upon complexation is expected due to the lose of coordinated aqua ligand (Table 2).

The integrity of the intercalated ligands and/or metal complexes structure is confirmed by the FTIR bands summarized in Table 3. The presence of strong, sharp bands at ~1616 and ~1384 cm^{-1} in the FT-IR spectra of the intercalated material is due to the formation of carboxylate anion. This is the result of ionization moiety in aqueous solution. These two absorption bands actually belong to asymmetric and symmetric carboxylate stretching bands, respectively [15]. Whereas, the bands at higher frequency ~1680 cm^{-1} corresponding to the stretching vibration of unionized COOH. When the Zn/Al ratios are slightly greater than 2, a proportion of the carboxylic acid groups are deprotonated upon intercalative ion-exchange. The two hybrid materials exhibited very similar FT-IR spectra, no band was observed at about 827 cm^{-1} for the symmetric stretching mode v_1 of NO_3, indicating that the exchange reactions were completed (since this band is strong for the precursor $[Zn_2Al(OH)_6]NO_3.xH_2O$). The coordination of the carboxylate groups of the ligand to the metal ion is suggested by the red-shift or lower frequency of about ~16 cm^{-1} in the wave number between v_{as} and v_s of (–COO). This was more dominant when metal complex is introduced. The reduction might be due to coordination, which could be affected by the H-bonding between the intercalated complex and the hydroxyl of the layers [22]. Below 850 cm^{-1}, the FTIR spectra of the two LDHs contain some bands due to the guest species in addition to peaks arising from the host lattice. The C-N and the C-H stretching vibration are also observed at ~1105 and ~2930 cm^{-1}, respectively.

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Table 3. Summary of FT-IR Data and Assignment for LDHs Precursor, Pure Ligands, LDHs-Ligands and LDHs-Metal-Ligands Intercalates.

Material	Assignment				
	-CH	$-COO_{assym}$	$-COO_{sym}$	-CN	-AlOH
$[Zn_2Al(OH)_6]NO_3.xH_2O$	-	1635 (H_2O)	-	-	960
EDDA (H_2EDDA)	2969	1698	1398	1069	-
$[Zn_2Al(OH)_6(EDDA)].xH_2O$	2930	1615	1383	-	-
$[Zn_2Al(OH)_6](NiEDDA)_y.xH_2O$	2860	1610 (s)	1383	1104	965
$[Zn_2Al(OH)_6](CoEDDA)_y.xH_2O$	2890	1605 (s)	1389	1105	945
NTA (H_3NTA)	2991	1732	1434	1113	-
$[Zn_2Al(OH)_6(NTA)].xH_2O$	2933	1616	1384 (s)	1130	910
$[Zn_2Al(OH)_6](NiNTA)_y.xH_2O$	2885	1620 (s)	1383 (s)	1131	912
$[Zn_2Al(OH)_6](CoNTA)_y.xH_2O$	2884 (sh)	1617	1384 (s)	1128	910
EDTA (H_4Y)	2950	1695	1420 (s)	1136	-
$[Zn_2Al(OH)_6Y].xH_2O$	2960	1603	1383 (s)	1108	918
$[Zn_2Al(OH)_6](NiY)_y.xH_2O$	2969	1596 (s)	1385 (s)	1103	925
$[Zn_2Al(OH)_6](CoY)_y.xH_2O$	2933	1600 (s)	1390 (s)	1102	920
DTPA (H_5DTPA)	2926	1706 (s)	1351	1144	-
$[Zn_2Al(OH)_6$ (DTPA)].xH_2O	2970	1600 (s)	1386	1100	925
$[Zn_2Al(OH)_6](NiDTPA)_y.xH_2O$	2972	1597 (s)	1395	1098	925
$[Zn_2Al(OH)_6](CoDTPA)_y.xH_2O$	2971	1598	1399	1100	923

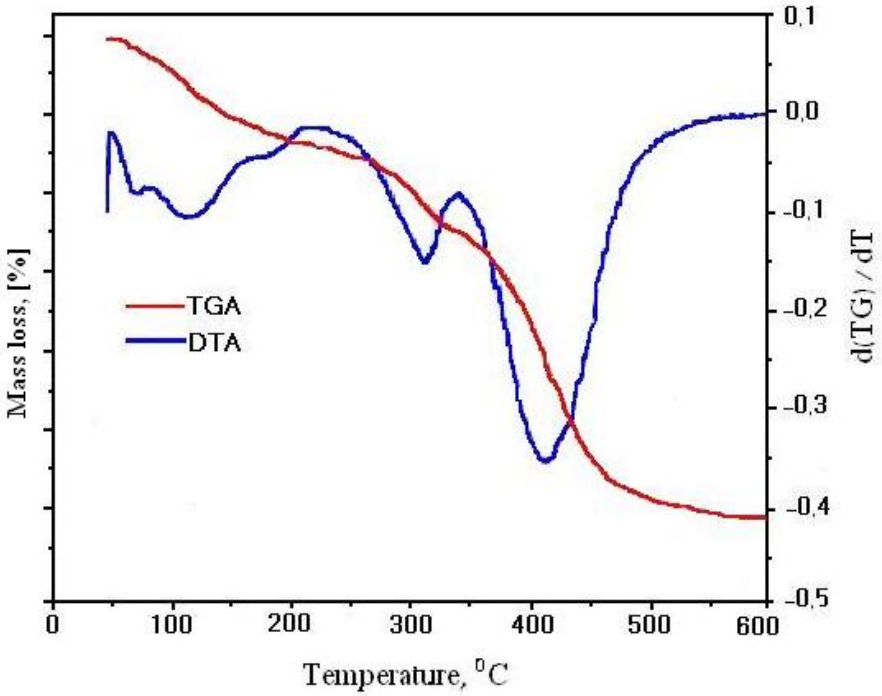

Figure 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for Zn_2/Al-edta intercalated compound.

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The results of the thermal study TG-DTA analyses for all the intercalated compounds show weight losses at similar temperature range which is classical to LDH intercalated compounds reported in literature [31]. The TG-DTA curve for one of the samples of Zn_2/Al-edta observed in (Fig. 2) show a series of continuous weight loss in the region 80-130^{0}C with an endothermic peak in the DTA curve at ~110^{0}C due to loss of surface adsorbed and interlayer water. The other endothermic effect at ~180-330^{0}C (DTA max at 310^{0}C) is due to the partial decomposition of the ligand and removal of trace co-intercalated CO_3^{2-}. The combustion of the intercalated ligand is observed, with the dehydroxylation of the Zn/Al layer and elimination of the intercalated guest as carbon dioxide along with the formation of Zn/Al mixed oxide. This is presented by the final endothermic effect recorded by the strong peak at 350~450^{0}C with major mass loss of (~35-40 wt.%) in the DTA curve under air atmosphere. Obviously, the thermal stability of the intercalated Zn_2Al-edta enhanced compared to the precursor salt [14], as well as for other guest ligands of edda, nta and dtpa following the order of increasing in number of carboxylic groups which subsequently increase the hydrogen bonding.

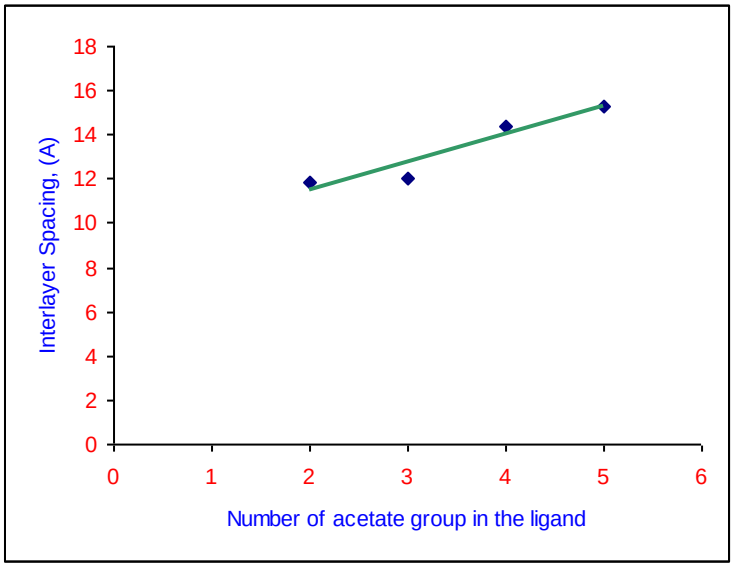

Figure 3. Interlayer spacing of the intercalated LDH, (Å) vs. the number of acetate groups (n) attached to the ligand.

The observed interlayer spacing and the number of acetate groups (n) attached to the different organic ligands gave an expected linear relationship (Fig. 3). A similar trend is observed by Newman et al [29], for dicarboxylic acid anions and d-spacing of LDHs prepared by coprecipitation. Another analogues trend is reported by Meny et al [32], for ZnCr-LDH containing a series of linear aliphatic monocarboxylates prepared by anion exchange. The interlayer spacing was found to increase linearly from 11.2 Å for (edda) (n= 2) to 15.31 Å for (dtpa) (n= 5).

4. CONCLUSIONS

Layered double hydroxide hybrids intercalated by anionic organic chelating ligands have successfully been prepared by two preparation methods of co-precipitation and ion-exchange. In order to further investigate the nature of Co(II) and Ni(II) intercalated complexes, two different routs were followed a direct incorporation of the ligand-metal complex and indirectly by forming the metal complex within the LDH layers. The intercalation of anionic metal complexes with the series of organic ligands

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that have different number of coordination sites those from EDDA to DTPA within the Zn_2Al layered double hydroxides was successfully synthesized. A comparison was made between the gallery height between the layers and the number of carboxylic acid groups of the ligand by PXRD. The materials may have applications in the field of separation and extraction reactions in addition to our next work on intercalating a pharmaceutically active azide compounds into the Zn_2Al layered double hydroxides in a view of studying the features of their functional groups and stability.

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The authors declare no conflict of interest

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