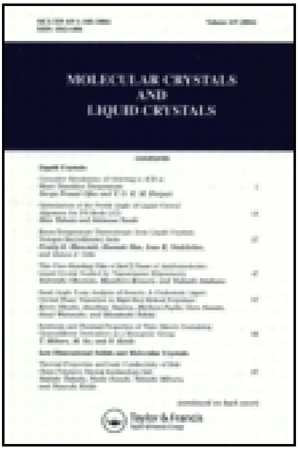

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Organic Bilayers Intercalated in Zinc(II)-Chromium(III) Layered Double Hydroxides

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Organic Bilayers Intercalated in Zinc(II)-Chromium(III) Layered Double Hydroxides

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The intercalation of three different anions derived from carboxylic acids is reported. It was shown that the intercalated anions of cholic and diphenylacetic acids form bilayers in the LDH interlamellar domain with different interactions involved in such arrangements. Each anion species showed the same interlayer arrangement for different Zn(II)/Cr(III) ratios, probably due to the intermolecular interactions that maintain the interlayer organization, independently of the available space per anion.

Keywords: Layered Double Hydroxides; Anionic Clays; Hydrotalcite; Diphenylacetic Acid; Diphenic Acid; Cholic Acid

I – INTRODUCTION

Layered Double Hydroxides (LDHs) [1] are a class of materials which have received great attention in the last years due to their wide range of applications derived from their properties. They can be used as catalysts and catalyst supports, polymer stabilisers, adsorbents and anion exchangers [2,3].

LDHs present a structure derived from that of brucite, a lamellar hydroxide in which Mg^{2+} cations are co-ordinated with hydroxide groups forming octahedrons that share edges, resulting in neutral charged layers. If some M^{2+} cations in the brucite structure are isomorphically substituted by M^{3+} cations, a positive residual charge results in the layers, which should be neutralised by anionic species intercalated between the layers together with water molecules [1,2]. A wide variety of organic compounds can be incorporated into the interlayer domain of LDHs [4], producing materials with relevant applications in different areas such as catalysis, selective adsorption, photochemistry and electrochemistry. An understanding of the factors controlling the interlayer arrangement is important if tailored applications in areas such as those mentioned above are to be explored for organo-LDHs [5]. Synthesis of several LDHs containing various M^{2+}, M^{3+} and anion combinations enable variations in the basal spacing, producing new compounds with features that combine the properties of the lamellar structure with those of the anions [3].

LDHs can be represented by the general formula:

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{m-}_{x/m}.nH_2O\ , \text{ where:}$$

M^{2+} represents a bivalent cation,
M^{3+} represents a trivalent cation,
A^{m-} represents the anion with charge m-.

The layer specific charge is directly related to the exchange ratio (x in the general formula that represents LDHs: $x = M^{3+} / (M^{2+} + M^{3+})$) of the trivalent cation [3].

This work is concerned with the intercalation of three different anions derived from carboxylic acids – cholic acid, diphenic acid and diphenylacetic acid - in LDHs with different Zn(II)/Cr(III) ratios. The aim of this study was to investigate the arrangement of the anions in the interlamellar domain and the molecular interactions involved in such arrangement.

II - EXPERIMENTAL

LDH synthesis was carried out at different Zn(II)/Cr(III) ratios (from 2 to 9) by the coprecipitation method at constant pH [2], where an aqueous solution containing the metal cations – 0.0833 mol of $Zn(NO_3)_2.6H_2O$ and 0.0167; 0.025; 0.050 or 0.075 mol of $Cr(NO_3)_3.9H_2O$ for the 2, 3, 6 and 9 ratios respectively - was dropped at a constant rate into the sodium salt anions aqueous solution, with the concomitant addition of a 2 mol dm^{-3} NaOH solution in order to keep the pH at a constant value (see table 1). The precipitates were filtered, washed with water and divided into two portions; the first was dried and the second was submitted to a hydrothermal treatment during 18 hours at 100 °C.

TABLE 1 Specific conditions for the sample synthesis

Sample	Zn/Cr ratio	pH
[Zn-Cr-Dpa]	2:1	7.0
[Zn-Cr-Dpa]	3:1	7.0
[Zn-Cr-Dpa]	6:1	7.0
[Zn-Cr-Dpn]	2:1	8.0
[Zn-Cr-Dpn]	3:1	8.0
[Zn-Cr-Dpn]	6:1	8.0
[Zn-Cr-Cho]	3:1	8.0
[Zn-Cr-Cho]	6:1	8.5
[Zn-Cr-Cho]	9:1	8.5

Dpa = Diphenylacetate; Dpn = Diphenate; Cho = Cholate

After the hydrothermal treatment, samples were washed, dried and characterised by PXRD using a Siemens D5005 X-ray diffractometer with a graphite monochromator selecting the Cu Kα radiation (1.5406 Å), in the 2θ range from 2 to 70°, with a step of 0.02° s^{-1}. FT-IR spectroscopy measurements were performed in KBr pressed pellets with 2% of sample using a Spectrophotometer Infra Red Nicolet Mod. Protégé 460, from 4000 to 400 cm^{-1}, with 60 scans per analysis. Thermal analysis was carried out using a TA Instruments SDT 2960 Simultaneous DTA-TGA equipment, in a synthetic air atmosphere

(80% N_2, 20% O_2), with a gas flux of 100 $cm^3 min^{-1}$, at a heating rate of 5 °C min^{-1}, from room temperature to 1000 °C.

III - RESULTS AND DISCUSSION

The PXRD patterns indicated the formation of crystalline and lamellar compounds for all intercalated anions, as shown in Fig.1. All the samples presented an increase in crystallinity after hydrothermal treatment, indicated by the increase in peak intensities. For the Zn-Cr-Dpa-LDH and Zn-Cr-Dpn-LDH, samples were prepared at Zn:Cr ratios of 2:1, 3:1 and 6:1, while for the Zn-Cr-Cho-LDH, they were prepared at ratios of 3:1, 6:1 and 9:1. In the case of cholate and diphenylacetate, the basal spacing found, 34.4 Å and 18.7 Å, respectively, was larger than the expected value, based on the molecular size estimated, using the *"PcModel for Windows, version 6.0 - Serena Software"*. The results can be attributed to the intercalation of a bilayer of these anions, in which the charged anion portions interact directly with the layers, while their chain tails (hydrophilic in cholate and hydrophobic in diphenylacetate) interact between themselves, originating stable arrangement.

Fig. 2 presents a schematic model proposed for the arrangement of the anions (a) Cho and (b) Dpa intercalated in Zn-Cr-LDHs. Different types of interaction between each intercalated anions - hydrogen bonding in the case of cholate and hydrophobic interactions in the case of diphenylacetate - play a crucial role in the arrangement of the anions, determining the basal spacing found in LDHs. If these interactions could produce different arrangements of the anion, several different basal spacings would be obtained for different layer charge densities.

In the case of cholate anions, the interactions occur directly between OH groups of adjacent molecules and/or over water molecules. These results show the possibility of the insertion of neutral molecules with some polar character, into the interlayer domain in the bulk of thee organic bilayer, with the possibility of varying the hydrogen-bonded networks, as reported by K. Nakano for organic guest in the crystal structure of cholate [6].

Phenyl groups of diphenylacetate anions are responsible for the intermolecular hydrophobic interactions in the interlayer domain, probably involving overlap of π orbitals of each non-polar group. In this case, unlike the case for cholate, insertion of a neutral molecule would be possible for guest molecules with a highly hydrophobic character.

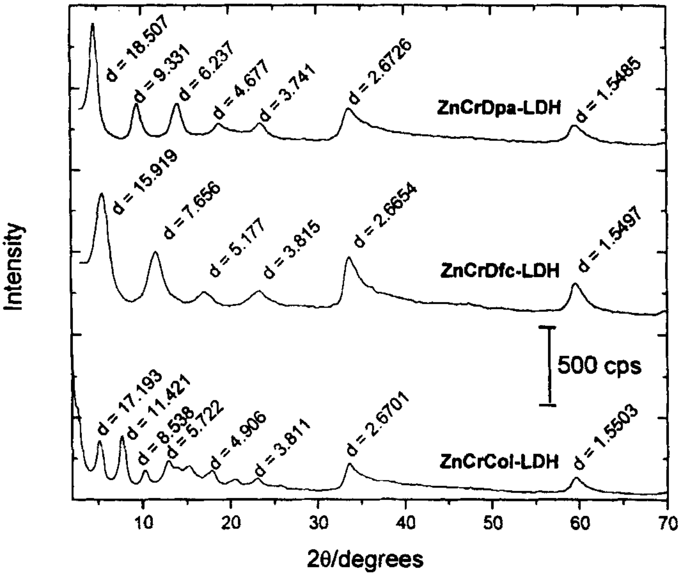

FIGURE 1 PXRD patterns of samples Zn-Cr-Dpa-LDH, Zn-Cr-Dpn-LDH and Zn-Cr-Cho-LDH at the 3:1 Zn(II)/Cr(III) ratio.

The fact that the variation of Zn(II)/Cr(III) ratio from 2 to 9 did not affect the basal spacing for each intercalated anion supports the idea that the interactions between organic chains play a decisive role in the arrangement of the anions in the interlamellar domain. These results show that the arrangement of the anions as bilayers in the interlamellar domain is not dependent on the area available per monovalent anion, but depends exclusively on the intermolecular interactions between the anions.

cited above. It was then attributed to the formation of a single anion layer in the interlayer domain, and, as expected, did not vary with the Zn/Cr ratio. Here, the basal spacing found, agreeing with that estimated for one anion, expresses the interactions of carboxylate groups of such anion with the layers. The variation in layer charge density did not affect the arrangement of the anions.

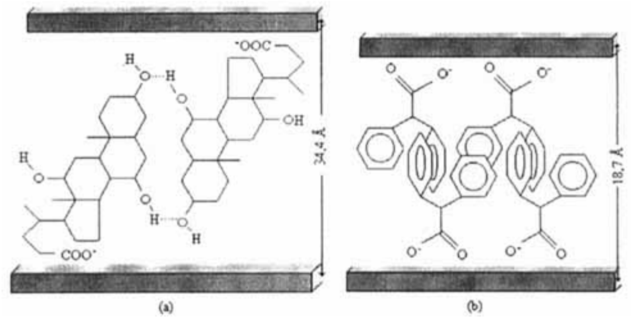

FIGURE 2 Schematic representation of the anions Cho (a) and Dpa (b) forming an anion bilayer in the interlayer domain.

Similar thermal decomposition behaviour was observed from the TGA/DTA curves for materials containing the same anion in different Zn/Cr ratios. However, a shift in the decomposition temperature of the organic species was observed by varying the charge density. The greater the charge density, the higher the thermal stability of the organic species. Fig. 3 shows the TGA/DTA curves for the Zn-Cr-Dpa-LDH LDH at the 3:1 Zn(II)/Cr(III) ratio.

The transition observed in the interval from ambient temperature to approximately 200 °C is due the water loss from the sample. The step from 200 °C to approximately 400 °C is assigned to the organic decomposition in each system, together with the hydroxyl groups. Zn-Cr-Cho-LDHs showed the highest final decomposition temperature, probably due to the major complexity of this intercalated organic species compared to the others.

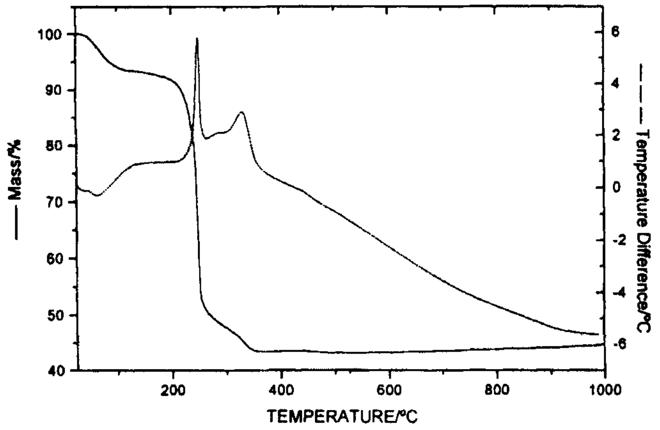

FIGURE 3 TG/DTA curves for Zn-Cr-Dpa-LDH LDH at the 3:1 Zn(II)/Cr(III) ratio.

The IR spectra obtained did not show differences for the same system when charge density was changed. Fig 4 presents spectra of LDHs intercalated with the three anions, Cho, Dpa and Dpn, in a 3:1 Zn(II) /Cr(III) ratio. In all of the spectra it was possible to identify an intense and broad band around 3400 cm^{-1} due to the hydroxyl groups in the layers and water molecules. Also, the bands due to the carboxylate group, around 1590 and 1380 cm^{-1}, were observed for all samples. For the cholate anions, the bands relative to the alcohol groups in the molecule can be identified near 3000 cm^{-1}. The absence of bands at around 1340 cm^{-1} indicated the absence of nitrate anions.

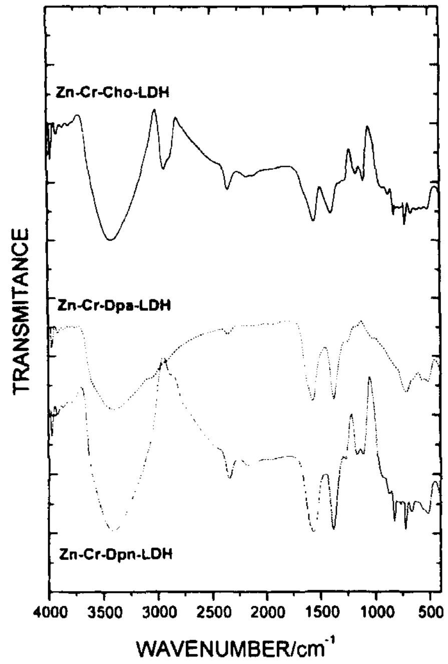

FIGURE 4 FT-IR spectra for systems Zn-Cr-Cho-LDH, Zn-Cr-Dpa-LDH and Zn-Cr-Dpn-LDH at the Zn(II)/Cr(III) = 3:1 ratio.

IV – CONCLUSION

Cholate, diphenylacetate and diphenate anions were intercalated in LDHs of the Zn-Cr system giving crystalline materials with a basal spacing of 34.4 Å, 18.7 Å and 15.5 Å, respectively. In the case of cholate and diphenylacetate anions, these results can be attributed to the intercalation of the organic anion in bilayer arrangements. The interactions involved in each case play a fundamental role in the final arrangement of the anions in the interlamellar domain and consequently, in the basal spacing of LDHs. This is supported by the fact that the variation of the layer charge density did not affect the arrangement of anions in the interlayer domain. By controlling these interactions, it would be possible to modify the interlayer anions arrangement in order to use these materials in different applications in the areas previously mentioned for organo-LDHs.

The Zn-Cr-Cho-LDHs showed the highest final decomposition temperature when compared with the other systems. This result may be due to the greater difficulty in disrupting the interactions involved, in completing the thermal decomposition of this anion.

FT-IR data confirm the presence of the intercalated anions with the characteristic bands of their chemical groups. A more detailed study on the interactions involving the intercalated anions will reveal some interesting properties of these materials.

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