

## Azoic dyes hosted on hydrotalcite-like compounds: Non-toxic hybrid pigments

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### Abstract

Layered double hydroxides with the hydrotalcite type structure and a Mg:Al ratio of three have been prepared with an azoic dye (methyl orange) stabilized on the external surface. Methyl orange was incorporated by reconstruction from a mildly calcined LDH-CO<sub>3</sub> precursor. The solids have been characterized by powder X-ray diffraction and FTIR, UV-vis and <sup>27</sup>Al, <sup>13</sup>C CP/MAS NMR spectroscopies. Hartree–Fock calculations were performed in order to investigate the guest-host arrangement. Results show that the methyl orange molecule is in configuration trans and that the carbons in  $\alpha$ - and  $\beta$ -positions, relative to the azo group, are interacting directly with brucite-like layers. Hydrotalcite shows a very high affinity for retention of azoic dyes. Another advantage offered by the stabilization of methyl orange anions in hydrotalcites compounds is that they are shielded from acid attacks.

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### 1. Introduction

In his book, *Il libro dell'Arte*, the Tuscan painter Cennino Cennini [1] talks about the preparation of materials for painting on fresco and on panel. He said “working up the colours and painting with them is the ‘glory of the profession’” [2].

Cennini proposed pigments highly specific for a determined surface and described the preparations of pigments from a variety of sources. The book reflected the necessity to find combinations of materials, both synthetic and natural, and use them as colorants. In particular, the pigments of the ultramarine blue group have been the subject of

much study. Literally, ultramarine blue means from “beyond the sea.” Such pigments consist of polysulfide anions encapsulated in the sodalite-like structure [3,4]. Cennini extracted it from the semi-precious stone, lapis lazuly, and invariably described it as more expensive than gold. The painting “Coronation of the Virgin” by Lorenzo Monaco, exhibited in the National Gallery of London, was painted with some ultramarine blues [2]. In antiquity, ultramarine blue was a luxurious and expensive pigment. The research done on these materials permitte these pigments to become commercially available and more research is now encouraged in order to enrich this family of pigments.

During the past decade a growing application of dyedoped materials was established. As a consequence, an increasing number of studies about this subject were published. Several synthesis strategies for the preparation of chromophores in porous silica, zeolites, and clays are described. Incorporation of dyes in inorganic matrices

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has been achieved by several methods, e.g., sorption from solution [5,6], sorption by solid-state reaction [7], covalent grafting [8–10] and in situ dye synthesis in nanopores [7,11]. Dye–inorganic compounds have found applications in the fields of optics, art (picture conservation) and food processing, among others [12,13]. Several factors have been reported to be determining in the properties of the dye–inorganic compound system. It is clear that, on the one hand, chemical properties such as polarity and acidity of the inorganic hosts, and on the other hand, the arrangement of the guest organic molecules, are key parameters in the stabilization of chromophores in inorganic matrices. In the case of pigment preparation, the inclusion of chromophores into inorganic matrices offers important advantages, e.g. higher temperatures of degradation than isolated chromophores.

A famous organic–inorganic pigment is the Maya blue, which is the molecule indigo incorporated into the channels of palygorskite clay [14–16]. This pigment was used in Mexico, from VII to XVI century A.D. to decorate statues and wall paintings. Maya blue pigment was rediscovered by Merwin [15] in his explorations of the Temple of the Warriors in Chichén Itza (Yucatán, México). Several studies are reported about this pigment [17,18].

Maya blue and ultramarine blue are only two examples of fascinating pigments. The pigment industry requires new hybrid materials that are able to replace some actual inorganic pigments, which contain polluting transition metals like lead and mercury. Moreover, the incorporation of dyes in layered structures gives rise to new organic–inorganic pigments. To achieve this goal, cationic and anionic dyes are hosted in materials with negatively and positively charged layers, respectively. Thus, Layered Double Hydroxides (LDH) frequently called Hydrotalcite-like compounds [19], provide a potential tool to be explored them as a host of guest organic molecules. LDH consists of positively charged brucite like layers. In hydrotalcite aluminum and magnesium of the main hydroxide layer are disordered over one site, but retain the sixfold coordination as magnesium in brucite [20]. Carbonate anions are the most common anions intercalated between the layers of hydrotalcite. When LDH are heat-treated at 400–600 °C the formation of a mixed oxide, MgAlO, with periclase-like structure is promoted. If these mixed oxides are brought into contact with water or anion containing aqueous solution, restoration of the layered structure with ions in the interlayer proceeds. Anionic dyes are more abundant than cationic ones; therefore, the stabilization of these entities on layered double hydroxides is quite relevant. Few papers have been published concerning the incorporation of dyes in hydrotalcite-like compounds [21]. We started this work with the aim of stabilizing two azoic dyes, methyl orange and black eriochrome T, on the hydrotalcites-like compounds. In this paper, we present how such stabilization is achieved and that resulting hybrids present convenient properties to use as pigments.

## 2. Experiment

### 2.1. Preparation of materials

A layered double hydroxide (LDH) with Mg/Al atomic ratio of 3 was prepared by co-precipitation at pH 9, by slowly adding a 1 N solution of magnesium and aluminum nitrates and a 1 N sodium carbonate solution to a 0.1 N solution of Na<sub>2</sub>CO<sub>3</sub>. The resulting solid was washed with distilled water and then dried at 80 °C for 8 h. A hydrotalcite-like structure was confirmed by X-ray diffraction, this sample is referred to as LDH-CO<sub>3</sub>. The LDH was calcined at 600 °C and the corresponding mixed oxide, Mg–Al–O, was obtained.

Methyl orange (MO) containing LDH was obtained when 0.33 g of mixed oxide Mg–Al–O was put in contact with 25 mL of 0.006 M methyl orange solution for 2 h. Then, orange solids were separated from uncoloured liquids by centrifugation and dried at 80 °C. This solid was labeled LDH-MO.

It is well-known that methyl orange (4-[4'-dimethylamino]phenylazo]-benzenesulfonate) is an acid–base indicator. In order to take advantage of this property, another sample of methyl orange containing layered double hydroxide was prepared. This time, the methyl orange containing solution was acidified at pH 1 by adding HNO<sub>3</sub>. Then, the same adsorption procedure was followed as with preparation of LDH-MO. At the start, the solution was red. However, after adding mixed oxide Mg–Al–O, the suspension recovered its orange colour. In order to maintain acid pH, HNO<sub>3</sub> was added during the reconstruction of the layered structure. However, the pH changed immediately to neutral value (7.2). The sample prepared under acid conditions was named LDH-MO(Ac).

Finally, another LDH containing MO was prepared when MO and LDH-CO<sub>3</sub> were mechanically mixed (MO content 4.9% wt) and heated at 200 °C for 4 h. This sample was named LDH-MO(Mix).

The preparation of MO-LDH materials was carried out in a CO<sub>2</sub> free atmosphere. In order to avoid the sorption of CO<sub>2</sub>, the samples were characterized immediately after preparation.

### 2.2. Characterization

The materials were characterized by X-ray diffraction (XRD) and infrared (FTIR), solid-state nuclear magnetic resonance (NMR) and ultraviolet–vis (UV–vis) spectroscopies.

The Powder XRD patterns were recorded in a Siemens D500 instrument using Cu K<sub>α</sub> radiation.

The FTIR spectra were acquired as KBr pellets at 2 cm<sup>-1</sup> resolution at room temperature on a Perkin-Elmer 1600 series-FTIR spectrometer, equipped with a DTGS detector.

The UV–vis spectra were recorded in a Perkin-Elmer Lambda 40 UV–vis spectrometer in the spectral window from 600 to 300 nm.

The solid-state  $^{13}\text{C}$  CP MAS NMR spectra were obtained at a frequency of 75.422 MHz on a Bruker ASX 300 spectrometer using a 4 mm cross-polarization (CP) MAS probe with a spinning rate of 8 kHz. Typical  $^{13}\text{C}$  CP MAS NMR conditions for the  $^1\text{H}$ – $^{13}\text{C}$  polarization experiment used a  $\pi/2$  pulse of 4  $\mu\text{s}$ , a contact time of 1 ms, a delay time of 5 s, and 16,000 scans. Chemical shifts were referenced to solid adamantane shift at 38.2 ppm relative to TMS.

The  $^{27}\text{Al}$  MAS NMR spectra were obtained operating the spectrometer at a resonance frequency of 78.15 MHz. The samples were spun at 10 kHz. A single pulse of 2  $\mu\text{s}$  with a repetition time of 0.5 s was used. Chemical shifts were referenced to an aqueous  $\text{AlCl}_3$  solution.

### 2.3. Methyl orange desorption

Methyl orange containing LDH were tested for MO desorption by shaking them in contact with water and solutions enriched with anions, such as chlorides and carbonates, for 2 h. The samples were washed six times: two times with  $\text{H}_2\text{O}$ , two times with 1 M NaCl solution, and two times with 1 M  $\text{Na}_2\text{CO}_3$  solution. Solids and liquids were separated by centrifugation and then the MO desorbed was quantified in solutions by UV–vis spectroscopy by interpolating intensities measured in a calibration curve previously drawn.

### 2.4. Theoretical calculations

The molecular geometry of an isolated methyl orange anion in the ground state was calculated by using the ab initio Hartree–Fock method [22] with 6-31G and 3-21 G as the base set. Three configurations were considered: the *cis*-form and two *trans*-forms. The first *trans*-form considers aromatic rings in the perpendicular planes and the second *trans*-form considers aromatic rings in same plane.

## 3. Results

The MO content in various LDH solids, as determined by chemical analyses, is reported in Table 1. MO uptaken was close to MO put in solution during the preparation step. This was expected because at the end of the dye incorporation there was a suspension composed of an orange solid and a colorless liquid.

X-ray diffraction patterns displayed in Fig. 1 show the evolution from LDH- $\text{CO}_3$  to LDH-MO: the layer structure of LDH- $\text{CO}_3$  is destroyed by heating it at 600 °C, resulting

Table 1  
Methyl orange content on the various LDH-MO

Sample	MO content (wt.%)
LDH-MO	5.6
LDH-MO(Ac)	5.1
LDH-MO(Mix)	4.9

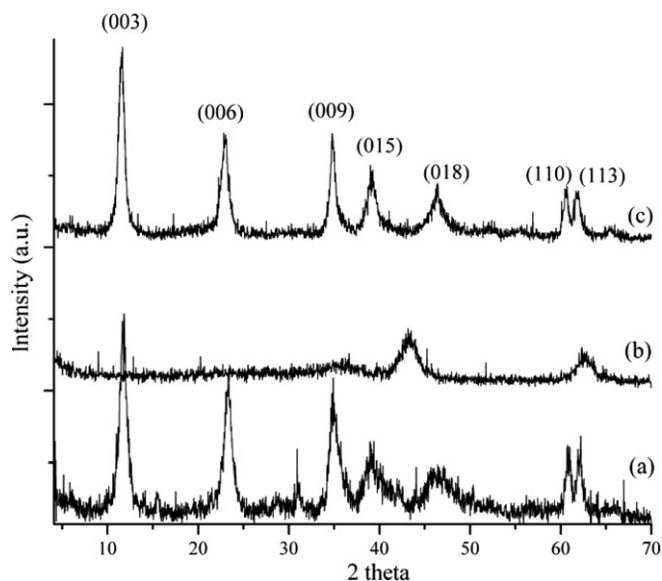


Fig. 1. X-ray diffraction patterns: (a) LDH- $\text{CO}_3$ , (b) LDH- $\text{CO}_3$  calcined at 600 °C and (c) LDH-MO. Numbers above peaks correspond to Miller index (hydrotalcite, JCPDS file).

in mixed oxide MgAlO (periclase like structure) as the peaks at 43.3 and 62.8 in  $2\theta$  scale were clearly resolved. This mixed oxide recovers the layer structure if it is put in contact with a methyl orange solution.

Interlayer distance was calculated for LDH samples from  $d(003)$  spacing [23], Table 2. Interlayer distance increases slightly in LDH-MO and LDH-MO(Ac) samples compared to LDH- $\text{CO}_3$ . No significant differences were observed in interlayer distance values corresponding to LDH- $\text{CO}_3$  and LDH-MO(Mix) samples.

Fig. 2 shows the FTIR spectra at room temperature of LDH- $\text{CO}_3$  and MO containing LDH samples. In the spectrum of LDH- $\text{CO}_3$  the characteristic absorption bands due to interlayer carbonates anions are observed. The bands at 1420 and 1370  $\text{cm}^{-1}$  are assigned to two asymmetric  $\nu(\text{CO})$  stretch,  $\nu_3$ , bands for free carbonate ion in  $D_{3h}$  symmetry. There is an appearance of two bands rather than one. This is due to the loss of  $D_{3h}$  symmetry [23–25]. In the spectra of regenerated MO containing regenerated LDH (spectra b and c) a single  $\nu_3$  band is observed. This indicates that a rearrangement of remaining carbonates occurred [23]. The band at 1490  $\text{cm}^{-1}$ , observed in spectra of LDH- $\text{CO}_3$  and LDH-MO(Mix), should be ascribed to nitrate species monodentate coordinated to the LDH surface [26]. These nitrates are present from synthesis of LDH- $\text{CO}_3$ .

Table 2  
Interlayer distance calculated from position of peak 003 in the XRD patterns

Sample	Interlayer distance (Å)
LDH- $\text{CO}_3$	7.529
LDH-MO	7.633
LDH-MO(Ac)	7.631
LDH-MO(Mix)	7.527

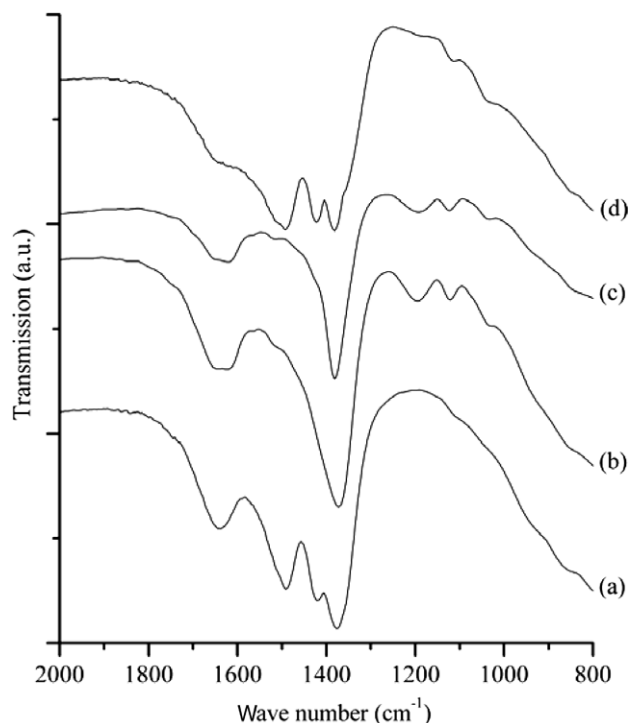


Fig. 2. FTIR spectra: (a) LDH-CO<sub>3</sub>, (b) LDH-MO, (c) LDH-MO(Ac) and (d) LDHMO(Mix).

Obviously, the band of nitrates does not appear in spectra of the LDH-MO and LDH-MO(Ac), as these samples were obtained from regeneration of Mg–Al–O oxides, then nitrates are eliminated in the calcinations step. The bending mode of interlayer water is found close to 1620 cm<sup>-1</sup> in spectra for all samples.

The bands at 1197, 1125 and 1045 cm<sup>-1</sup> in samples loaded with MO may be assigned to C–H, C–N and S=O vibrations, respectively [27]. These bands correspond to absorptions of chemical functions present in the methyl orange molecule, Fig. 3.

On the other hand, LDH containing MO, independently on the preparation procedure, presents the same absorption in the spectra UV–vis, Fig. 4. Visually, LDH-MO and LDH-MO(Ac) solids were orange, more luminous, and shinier than pure methyl orange.

Fig. 5 includes <sup>13</sup>C CP/MAS NMR spectra of MO, in two forms, pure and incorporated in LDH. From these spectra it was confirmed that incorporating MO in LDH does not cause significant changes in the structure of

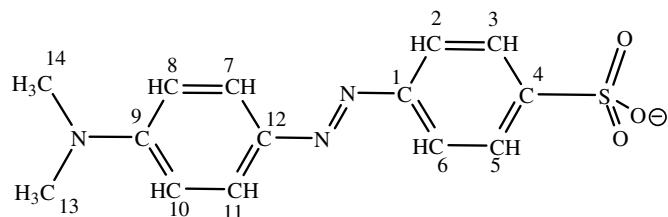


Fig. 3. Methyl orange anion structure (non-optimized). Numbering of carbon atoms to attribution of <sup>13</sup>C NMR peaks, Table 3.

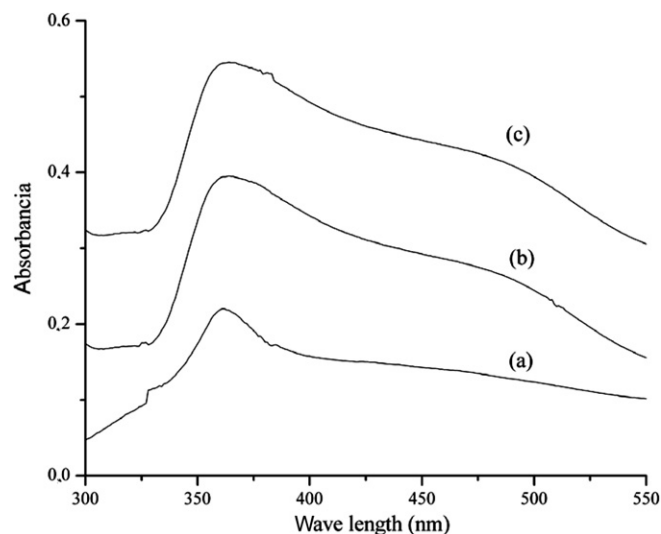


Fig. 4. UV–vis spectra recorded on thin self-supporting wafers of samples: (a) LDHMO(Mix), (b) LDH-MO and (c) pure MO.

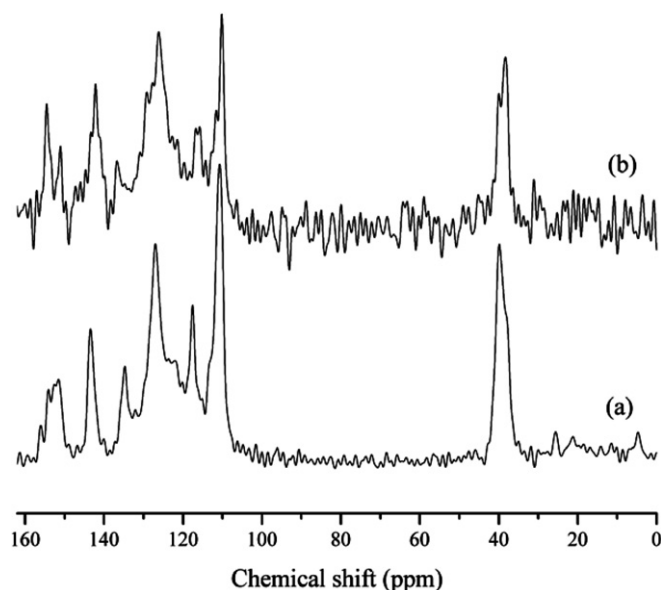


Fig. 5. <sup>13</sup>C CP MAS NMR spectra: (a) pure methyl orange and (b) methyl orange containing LDH (sample LDH-MO).

MO. Table 3 contains the assignation of peaks [28]. Carbons were numerated following the drawing in Fig. 3. It has been found that the peaks of carbons numbered 4, 7, 8 and 12 are clearly altered when MO is incorporated in LDH. The resonance for the carbons 4, 8 and 12 is shifted to up field in 2.1 ppm. Resonance of carbon 7 is shifted 1.9 ppm to down field. Peaks attributed to resonances of methyl, carbons 13 and 14, remain almost unchanged in regards to their position and intensity. Alteration of other signals is not clear because the signal/noise ratio is very low.

No significant differences were observed in <sup>27</sup>Al MAS NMR spectra displayed in Fig. 6 showing that LDH, free



Table 3  
Assignment of  $^{13}\text{C}$  NMR peaks in spectra exhibited in Fig. 5

Carbon <sup>a</sup>	Chemical shift, $\delta$ (ppm)	
	Pure methyl orange	Methyl orange on LDH
1	151.0	150.8
2	129.0	129.0
3	127.1	126.2
4	143.2	141.9
5	127.1	126.2
6	129.0	129.0
7	134.7	136.6
8	117.5	115.8
9	110.5	110.4
10	154.6	154.6
11	110.5	110.4
12	117.5	115.8
13	39.0	39.0
14	39.0	39.0

<sup>a</sup> Numbering of carbon atoms from Fig. 3.

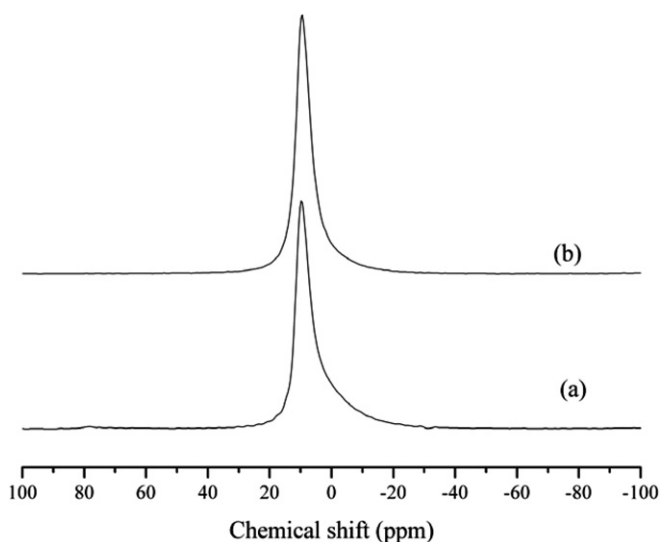


Fig. 6.  $^{27}\text{Al}$  MAS NMR spectra of LDH- $\text{CO}_3$  and LDH-MO samples, (a) and (b), respectively.

or loaded with MO, presents only one resonance at 5 ppm, due to octahedral ( $\text{Al}^{\text{VI}}$ ) aluminium species [29].

Methyl orange was desorbed from the samples when shaking them with water and solutions containing anions (chlorides or carbonates). Curves displayed in Fig. 7 show the amount of MO retained in the solids after leaching. Note that, in LDH-MO and LDH-MO(Ac) samples, water causes a small amount of dye to leach.

In the LDH-MO(Mix) sample, however, a high amount of MO is released. It was also interesting that only a small amount of MO leaches when solids are washed two times with solutions containing chlorides and two times with carbonates solution.

Similar trends are observed in the amount of MO retained in LDH-MO and LDH-MO(Ac) samples: after leaching a very high amount (99%) of MO remains when they are washed only with water and close to 80% of MO

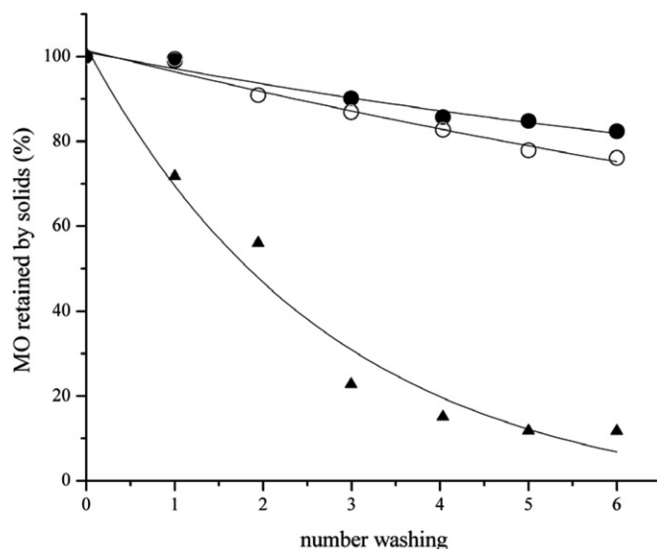


Fig. 7. Methyl orange retained by the solids after washing. ●- LDH-MO, ○- LDHMO(Ac), ▲- LDH-MO(Mix). Washing 1 and 2 with water; Washing 3 and 4 with NaCl 1 N; and washing 5 and 6 with  $\text{Na}_2\text{CO}_3$  1 N.

Table 4  
Total energy of methyl orange anions in the ground state

Basis set	Energy of optimized structures (Hartree)		
	<i>Cis</i>	<i>Trans</i> (planar)	<i>Trans</i> (non-planar)
3-21G	-1316.34823031	-1316.38975890	-1316.21768630
6-31G	-1323.06093716	-1323.09833862	-1322.92724509

is retained if solids are treated with chlorides and carbonates. In contrast, the sample LDH-MO(Mix) retains 56% of MO if washed with water and after lixiviation with chlorides and carbonates, solids retain only 10% of the initial amount of MO.

Table 4 shows the energy of isolated Methyl orange molecule calculated by ab initio Hartree–Fock method. Three configurations, Fig. 8, were considered: *cis*-form with two aromatic rings forming an angle of  $55.9^\circ$ , Fig. 8a, *trans* non-planar with two aromatic rings forming an angle of  $90.2^\circ$ , Fig. 8b, and *trans* planar with two rings in the same plane, Fig. 8c. In both base sets, the *trans* planar form appears to be the most stable configuration.

#### 4. Discussion

Mg–Al–O mixed oxides obtained from calcinations of LDH- $\text{CO}_3$  precursors may recover their layered structure easily by putting them in contact with solutions containing MO. In contrast, it is difficult to incorporate protonated MO species in HMO because of the base character of mixed oxides, Mg–Al–O, which acts as Lewis base in the reaction of Scheme 1.

The reaction is selective to form LDH-MO, not LDH-HMO, because HMO loses the proton easily,  $\text{p}K_a = 3.46$ , [30] when it is in contact with Mg–Al–O. Then, HMO

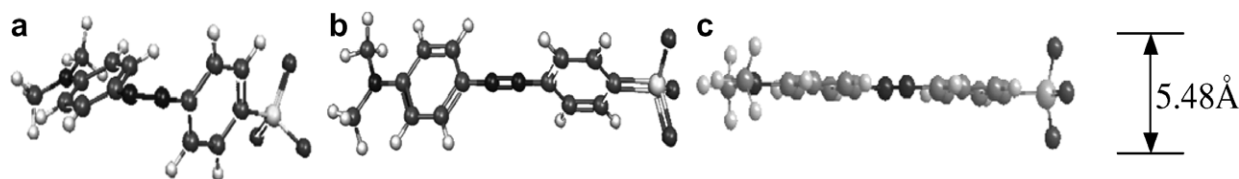
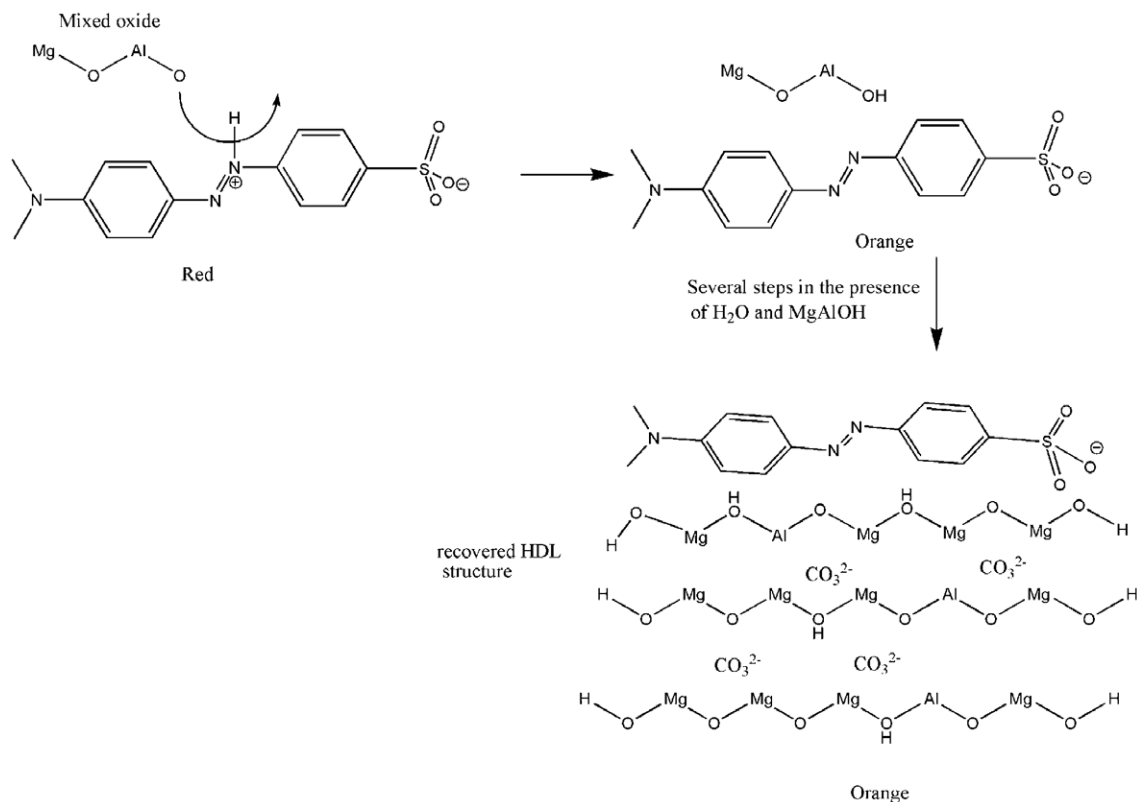


Fig. 8. The three isomorphs of the methyl orange anions, considered in the Hartree–Fock calculations. (a) *Cis*-form, (b) *trans*-form (distorted or non-planar) and (c) transform (planar).



Scheme 1. Chemical scheme of deprotonation of HMO by mixed oxides, Mg–Al–O, in the process of reconstruction of layer structure of LDH, memory effect.

species, which are responsible for the red colour in the solution, disappear rapidly and can not be incorporated in LDH structures. It should be emphasized that during the attempt to synthesize LDH with HMO,  $\text{HNO}_3$  was added in order to maintain acid conditions. However, a suspension containing LDH and MO rapidly recovered neutral pH. Thus, a first conclusion emerges: LDH–MO resists acid attacks because LDH acts as a base that neutralizes the acid.

A second result that should be discussed is the interlayer distances in the various solids. From Figs. 1 and 2 it is stated that the interlayer distance of MO containing LDH are close to those for LDH– $\text{CO}_3$ , in fact, only a small increase of 0.3 Å is seen. Such interlayer distances offer two possibilities: the first one is an arrangement in which the main plane of MO anions is parallel to the layers, and the second one is the incorporation of MO only on the external surface of LDH crystals.

Indeed, the interlayer distance may be determined by the  $\text{SO}_3$  group as shown by the structures drawn from Hartree–Fock calculations, Fig. 8. However, although the trans planar configuration of the molecule seems to be the most stable (Table 4) at this point it is not possible to discard any configuration of the molecule calculated by the Hartree–Fock method.

Nevertheless, such configurations of MO claim, at least, 5.48 Å of the layer space which, added to the thickness of a layer (ca. 4.4 Å), leads to a minimum interlayer distance of 9.9 Å. Anything higher than this distance was not observed (Table 2). Then, a second conclusion can be stated: MO is not incorporated in the interlayer space, but rather on the external surface of the LDH crystals. This result agrees with those reported previously, by Constantino et al. [5] showing that intercalation of MO into LDH takes place only at higher concentrations of MO than those used in

the present work. Then, in our experiments, the recovered layered structure is due to the water effect as observed in previous works [31–33]. Indeed, this structural memory effect of hydrotalcites occurs because of calcined hydrotalcites (periclase-like structure) turns out to be an ideal precursor for obtaining well-crystallized pure rhombohedral hydrotalcite. Stanimirova et al. pointed out that the regeneration of layered structure of hydrotalcites from periclase-like structures takes place through crystallization from solution [34]. Thus, interlayer space is occupied by hydroxyl anions and carbonates not eliminated in the calcination of LDH-CO<sub>3</sub>.

Concerning the configuration of dye entities on the LDH host, NMR results show that carbons in position  $\alpha$  and  $\beta$  relative to the azo group appear to be interacting with the external layers of LDH crystals. On the basis of these results the following model can be suggested, Fig. 9: Two direct interactions of MO with LDH. The first occurs between aromatic hydrogens of MO anions and the lone pair of electrons in oxygen from brucite-like layers; the second occurs between the nitrogen atom of azo group and the aluminium centers. Such interactions explain the differences found in the <sup>13</sup>C CP/MAS NMR spectra (Fig. 5). Oxygen from hydrotalcite-like compounds induce paramagnetic effects on carbons  $\beta$  relative to the azo group and, as a consequence, a shift to resonance peaks to up-field is observed. In contrast, as a result of the interaction of the lone pair of electrons of nitrogen with aluminium centers, deshielding effects take place in the carbon in  $\alpha$ -position and its resonance peak shifts toward weaker fields. Such interactions are possible if the methyl orange anions are arranged in trans form and planar form, which is the most stable form predicted by Hartree–Fock calculations, Fig. 8, Table 4. Indeed Azuki et al. [22] have shown that

this configuration of methyl orange anions is also the most stable even when analyzing solvent effects.

It should be noted that LDH, free and loaded with MO, present only Al<sup>VI</sup>. This result would be rather surprising, as it has been reported that reconstructed LDH contains an important fraction of tetrahedrally coordinated Al cations [33,35,36]. However, the reconstructed samples in this work were calcined only one time and reconstructed in the presence of organic molecules that could be adsorbed on the Al<sup>IV</sup> sites.

The chemical stabilization of the dye–LDH system can be inferred from the leaching tests results: It can be established that MO has a high affinity to LDH, Fig. 7. Indeed, in samples LDH-MO and LDH-MO (Ac), the MO is strongly stabilized and it is not released when samples are treated with chlorides or carbonates because these anions have a high affinity to reach the interlayer space of LDH and the MO is adsorbed on the external surface. In contrast, when MO is incorporated to LDH by mechanical mixing, like in the case of the sample LDH-MO(Mix), dye is easily removed by washing with water as the MO is not adsorbed on the surface of LDH, but it is only physically mixed with the LDH-CO<sub>3</sub>. Note that this can be related to the dispersion of MO on the LDH surface: MO incorporation by LDH reconstruction propitiates the best dispersion of MO. In contrast, MO incorporation by mechanical mixing propitiates only the physical contact between large particles of MO and large particles of LDH.

Regarding UV–vis absorption of LDH-MO pigments, they all absorb the same wavelength (359 nm), which is also the absorption wavelength of pure MO. However, with incorporation of MO in LDH, a visual effect is achieved: LDH presents preferential orientations parallel to 001 plane. As a consequence, these materials reflect the light and these pigments seem to be more luminous and shinier than pure MO.

Thus far, we have shown how methyl orange can be stabilized on LDH surfaces. It remains to be seen if similar stabilizations take place with other dyes. In order to clarify this last point, we have repeated the experimental part, reported for LDH-MO, but this time we replaced methyl orange with eriochrome black T, EBT hereafter (see chemical structure in Fig. 10), thus obtaining purple solids.

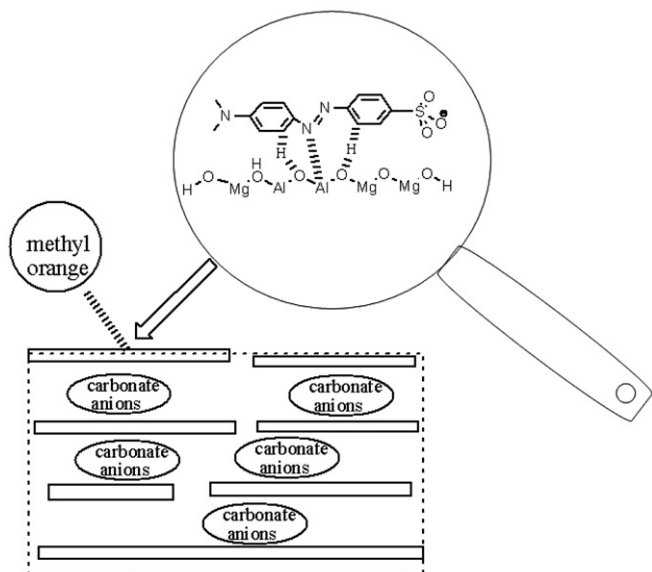


Fig. 9. Representation of interactions proposed as responsible of high affinity between the brucite-like layers and the methyl orange anions.

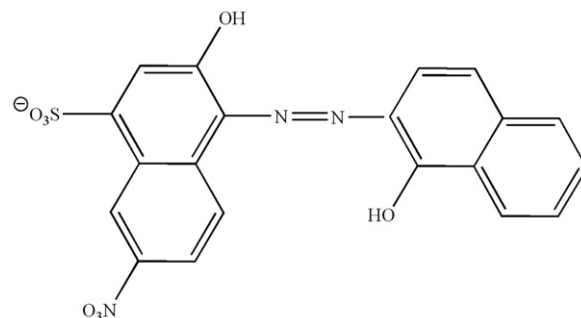


Fig. 10. Eriochrome Black T structure.

These LDH-EBT pigments presented similar properties to LDH-MO pigments, *i.e.* shielding from acid and alkaline attacks; shininess and luminosity.

For the sake of conciseness, the spectra and diffractograms from the LDH-EBT are omitted. However, it should be emphasized that similar results to those reported for LDH-MO have been obtained. These results point out that EBT interacts with the external layers of LDH structures, as shown for the LDH-MO system. Thus, a conclusion can be drawn: taking advantage of the memory effect from LDH, Azoic dyes can be stabilized on these structures to obtain organic-inorganic pigments. Furthermore, the wide variety of the azoic dyes could result in the production of a rich family of the azoic-dye-LDH pigments.

We have focused our study on the use of methyl orange and eriochrome black T anions adsorbed on hydrotalcite-like compounds as pigments. However, this is not the only potential application for these materials. The relatively small amount of chromophores stabilized on LDH structures often corresponds to the amount of active species in catalytic materials. Thus, the prepared materials may find application in photo-catalytic reactions.

Data on the sorption of methyl orange on external layers of hydrotalcite-like compounds reported in this paper show a procedure for direct retention of a secondary colour, orange, in a white inorganic matrix (LDH). However, other combinations of colours and matrices are possible.

## 5. Conclusion

Taking advantage of the memory effect of LDH, methyl orange and eriochrome black T are easily incorporated on these materials. Methyl orange anions are highly stabilized on the external layers of LDH crystals. Such stabilization is due to interactions between the aromatic carbons and nitrogen of the azo group from the azoic dyes with Al-O pairs from the brucite-like layers.

The azoic dyes-LDH materials present luminosity, shininess and resistance to acid, and alkaline attacks. These properties make them good materials as pigments. The colour of the pigments prepared can be easily fine-tuned as there is a wide variety of dyes available that can be hosted in LDH.

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