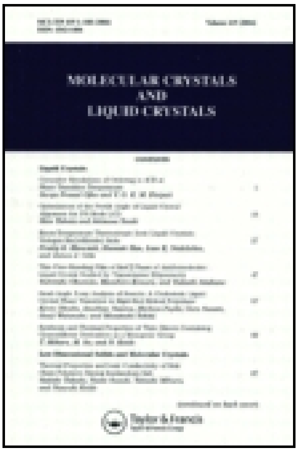

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Photoactivity of Cinnamate-Intercalates of Layered Double Hydroxides

Joao Valim [a], Benson M. Kariuki [a], John King [a] & William Jones [a]
[a] Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, England

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PHOTOACTIVITY OF CINNAMATE-INTERCALATES OF LAYERED DOUBLE HYDROXIDES

JOAO VALIM, BENSON M. KARIUKI, JOHN KING AND WILLIAM JONES
Department of Chemistry, University of Cambridge,
Cambridge CB2 1EW, England.

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Abstract The synthesis of photoactive (cinnamate) intercalates of layered double hydroxides is described. Corresponding single-crystal data on pure sodium salts enables information concerning the arrangement of the guest molecules within the hydroxide to be obtained.

Keywords: LDH, intercalates, cinnamates, photoactivity, NMR, powder x-ray diffraction

INTRODUCTION

Layered double hydroxides are an important class of materials consisting of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. In terms of charge they are mirror images of the extensively studied family of cationic clay minerals.[1] LDHs have application in the area of heterogeneous catalysis[2] (e.g. as carriers and as precursors to solid based catalysts[3]), as anion exchangers as well as supports for the controlled release of biologically active molecules.

A general representation of their structural formula is:

$$M_a^{2+}M_b^{3+}(OH)_{2a+2b}(X^-)_b.H_2O$$

where M^{2+} for example, can be Mg, Ni, Co, Cu or Zn; M^{3+} can be Al, Cr or Fe and X^- is generally CO_3^{2-} but may also be OH^-, Cl^-, or SO_4^{2-} A schematic illustration of the structure of the naturally occuring mineral hydrotalcite, which has the composition Mg-Al-CO_3-H_2O, is shown in Figure 1.[4]

Figure 2(a) illustrates a typical X-ray powder pattern from a laboratory synthesised LDH (in this case hydrotalcite). The repeat distance (d_{003}) corresponds to a gallery thickness of approximately 3 Å and is associated with the thickness of a carbonate anion. Calcination of the LDH (in air at 450 °C for 18 hours) generates a poorly crystalline product - Figure 2(b). This material - which may be considered to be a solid solution of Mg-Al-O in an approximate MgO matrix - has strong basic character and, as such, has itself been used as an effective solid base catalyst for a variety of reactions.[3] Exposure of the calcined material to carbonated water regenerates the original LDH - Figure 2(c).[5]

Of particular interest here, however, is the fact that if the calcined material is exposed to a decarbonated solution of organic anions, regeneration of the original LDH structure occurs with concomitant incorporation of the organic anion to yield an intercalated material.[6] Figure 3 illustrates the variation in gallery height which has been observed when a series of dicarboxylic acids are incorporated, in this way, into the gallery region. There is a linear relationship between gallery height and carbon number.

In this study, we have aimed at intercalating, *via* this calcined precursor route, variously substituted cinnamate anions. We have done so with the intention of studying the photochemistry of these molecules inside the gallery region. Given the well known solid state chemistry of cinnamic acid[7] we hope to be able to comment on the packing and reactivity of the guest molecules within the interlayer region. As part of this approach we have synthesised several sodium and magnesium salts of the cinnamate derivatives.[8] Some interesting comparisons may be made between the reactivity of (i) LDH -

intercalates, (ii) the corresponding salts and (iii) the corresponding acid in solution.

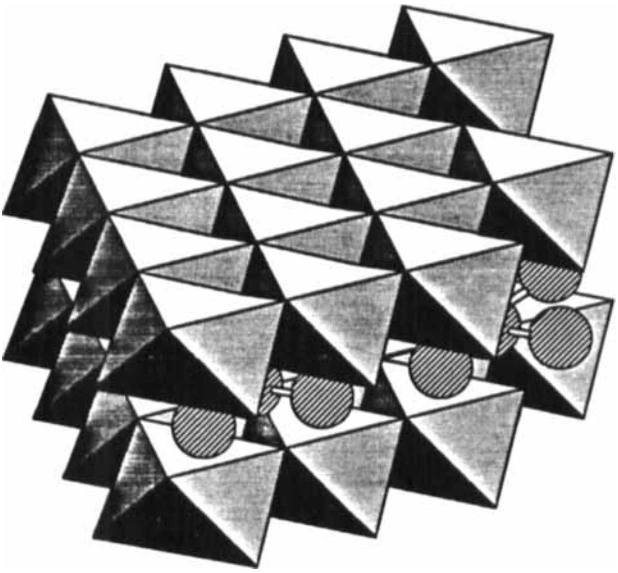

FIGURE 1 Schematic illustration of the naturally occurring hydrotalcite.

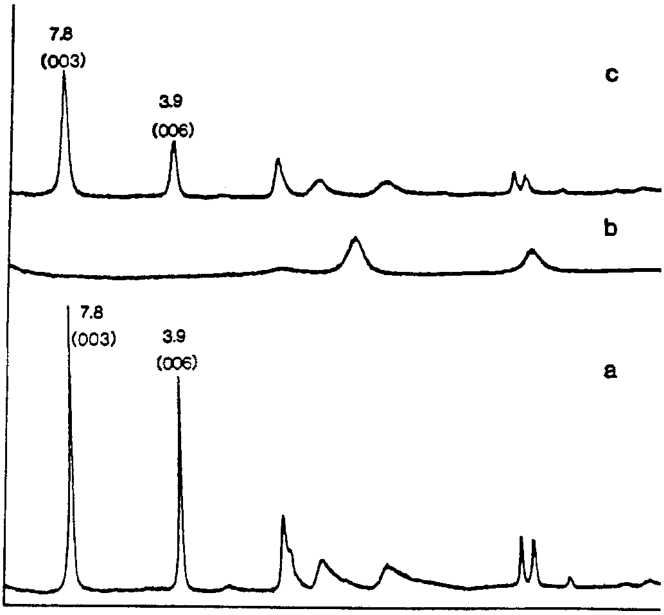

FIGURE 2 Powder XRD patterns from a) hydrotalcite b) calcined hydrotalcite and c) rehydrated hydrotalcite

EXPERIMENTAL

The LDHs and the method of intercalation has been described elsewhere.[6] Samples were irradiated with Pyrex filtered uv light using a 200 watt Hg lamp. ^{13}C solution NMR was used to identify the extracted organic component before and after uv irradiation. Single crystal measurements of the pure salts were made using an Enraf-Nonius CAD-4 diffractometer. For the intercalated materials the only crystallographic information which could be obtained was the gallery height using powder X-ray diffraction methods. We have studied the intercalates of *trans*-o-chlorocinnamate, *trans*-m-chlorocinnamate and *trans*-p-chlorocinnamate as well as corresponding sodium and magnesium salts.

RESULTS

Intercalated Materials

The gallery height of the original LDH with carbonate as the anion is 3.0 Å. After intercalation of the *trans*-o-chlorocinnamate anion this increases to 18.4 Å. Since the thickness of the brucite-like sheet is approximately 4.8 Å this indicates that the gallery height has increased to 13.6 Å. For the *m*-chloro derivative the gallery height is 14.0 Å and for *p*-chlorocinnamate the height is 15.0 Å.

Figure 4(a) illustrates the ^{13}C spectrum of p-chlorocinnamate after acid extraction from within the LDH and prior to uv irradiation. The spectrum is identical to that of the starting material.

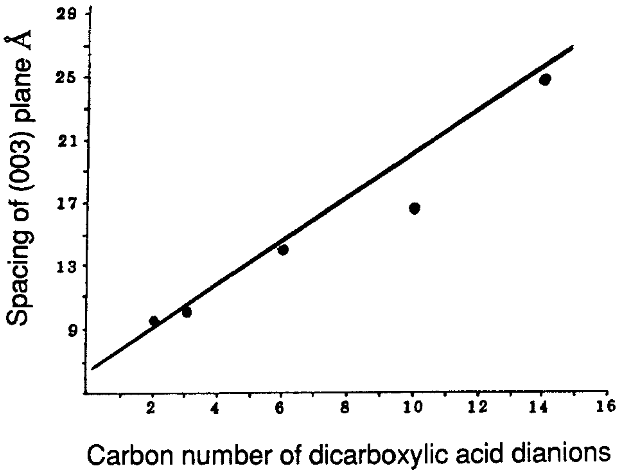

FIGURE 3 Variation in gallery height for various intercalated dicarboxylic acids.

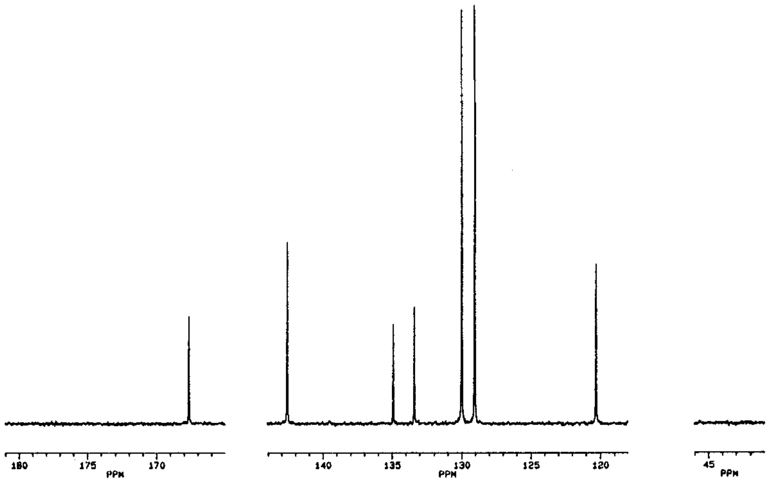

FIGURE 4 ^{13}C solution NMR spectrum of *p*-chlorocinnamate after acid extraction from within LDH but prior to irradiation.

After uv irradiation of the intercalate the acid-extracted material shows several additional peaks - see Figure 5. These, by comparison with the products from irradiation of the pure salts and of the solutions (see later) suggests that both dimerization and *cis* ↔ *trans* isomerization occurs within the gallery regions.

Crystalline Salts

The structures of two chlorocinnamate salts are examined - sodium *o*-chlorocinnamate dihydrate and sodium *p*-chlorocinnamate monohydrate. *o*-Chlorocinnamate exists in the space group $P2_1/c$, with cell parameters: a=14.506, b=3.733 and c=19.245 Å, β = 91.45°. Figure 6 shows the packing diagram of *p*-chlorocinnamate,[8] which exists in the space group $P\bar{1}$, with cell parameters: a=6.237, b=7.329 and c=21.438 Å, α=95.83, β=97.41and γ=89.53°. Both of these salt structures have the same basic form, which consists of hydrophilic sheets of co-ordinated metal cations lying on (001), and between these sheets are sandwiched two layers of the organic anion, arranged such that the hydrophilic portion of the anion is in contact with the cationic sheets, whilst the hydrophobic hydrocarbon portion of the anion is hidden on the inside, where the double layer is held together by van der Waals interactions.[8,9]

Comparing the separation of the cationic sheets with the basal spacing in the corresponding LDH intercalate yields:

	Crystal (001) spacing.	LDH basal spacing.
o-chlorocinnamate	19.3Å	18.4Å
p-chlorocinnamate	21.4Å	19.8Å

Thus, it may well be the case that the packing of the cinnamate anions is qualitatively similar in the LDH intercalate to that in the pure salt.

Calculation of closest double bond distances for each salt indicates that in the *o*-chlorocinnamate nearest neighbours are related by translation along **b**, giving a separation of 3.7 Å, whilst in the *p*-chlorocinnamate there are two reasonably short separations, each between two non-symmetry related anions stacked consecutively in the **b** direction and each with a separation in the region of 3.7 Å. Such a separation is well within the range expected to permit photodimerisation,[7] and indeed it is found that both of these salts undergo solid state dimerisation - see below.

Solid state activity:

Figure 7 shows the ^{13}C solution spectrum of crystals of sodium *p*-chlorocinnamate after uv irradiation. By comparison with the crystal structure analysis and spectra obtained from irradiation of the corresponding solutions (see below) we assign the additional peaks to the formation of photodimer.

Irradiation in Solution

When cinnamic acid derivatives are irradiated in solution it is known from numerous other studies that the principal reaction is of *cis* ↔ *trans* isomerization.[7] Figure 8 illustrates the spectrum obtained for *o*-chlorocinnamate. We assign the additional peaks to the *cis*-isomer.

DISCUSSION

Crystalline Salts

Whilst the difference in ring substitution between the two sodium salts is not marked, the difference in their detailed structures is quite significant in that they exist in different crystal systems and they possess radically different hydrophilic layers; the *p*-chlorocinnamate has edge sharing ribbons, which are linked into sheets by hydrogen bonding, whilst the *o*-chlorocinnamate has infinite edge sharing sheets.

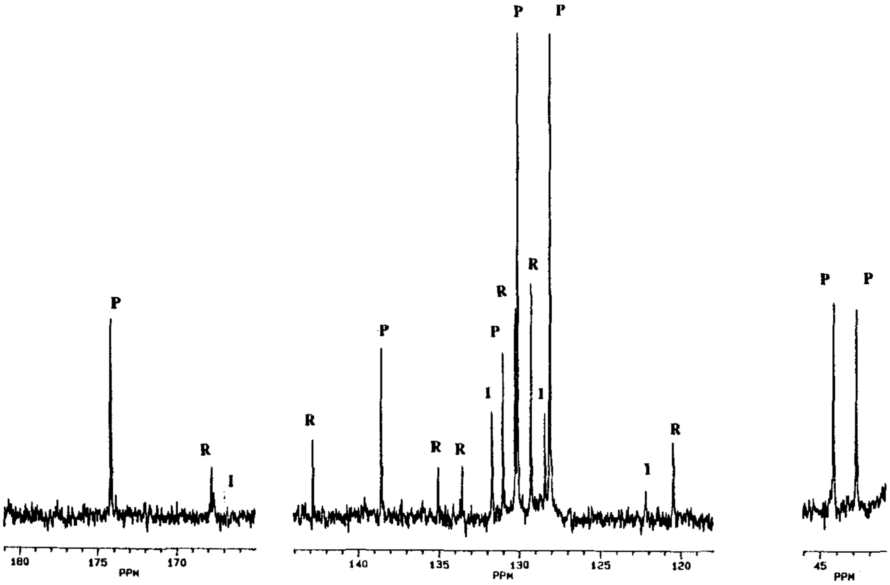

FIGURE 5 ^{13}C Solution NMR spectrum (CD_3OD) of *p*-chlorocinnamate following uv irradiation and after acid extraction from within the LDH. R = reactant; P = dimeric product; I = isomeric product (*cis*).

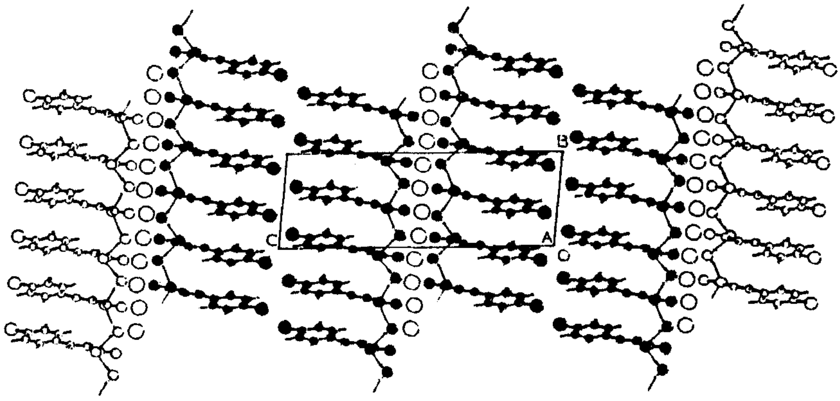

FIGURE 6 Sodium *p*-chlorocinnamate monohydrate viewed down the crystallographic x-axis. Photodimeric partners are stacked consecutively along the y-axis.

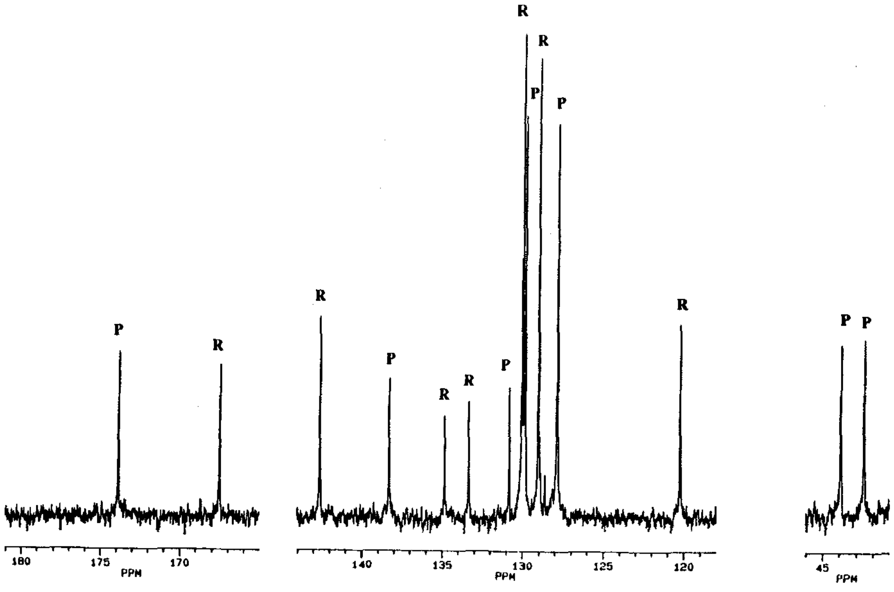

FIGURE 7 ^{13}C Solution NMR spectrum (CD_3OD) of *p*-chlorocinnamate from uv irradiated crystals of the sodium salt. R = reactant; P = dimeric product; I = isomeric product (*cis*).

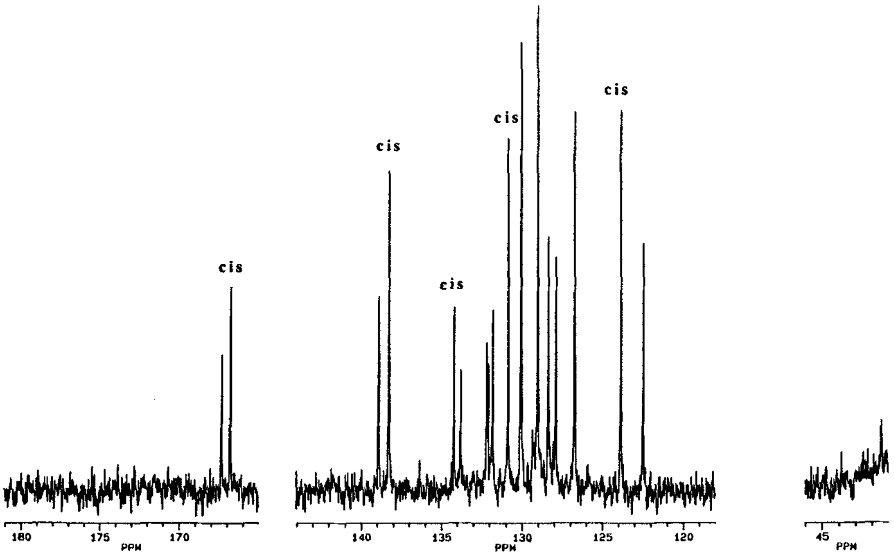

FIGURE 8 ^{13}C Solution NMR spectrum (CD_3OD) of *p*-chlorocinnamate after uv irradiation of an aqueous solution of the sodium salt.

It may, therefore, be possible to control the structure of the cation layer by controlling the number of waters of crystallisation which are present, or by varying the identity of the cation; there may, therefore, be an ability through this route to control the detailed disposition of anions and thus the photochemistry of a particular organic species.

Intercalates

Some points of comparison to the salts are noteworthy:

i) The packing density of the anions in the LDH will be a function of the Mg/Al ratio, and may be considerably lower than in the pure salts.

ii) Whereas in LDHs the hydrophilic layers consist of infinite sheets of edge sharing octahedra, this is not necessarily the case for the salts.

iii) In LDHs it is assumed to be the case that the metal cations remain co-ordinated by six hydroxyl groups (as is the case in brucite). It is found in the sodium salts, however, that the anions are directly co-ordinated to cations.

CONCLUDING REMARKS

We summarise here the main points.

(i) Photoactive intercalates of layered double hydroxides may be readily obtained.

(ii) Both photodimerization and photoisomerization of cinnamate anions occurs within the gallery region. It is likely that the relative amounts of isomerization and dimerization will be dependent upon the stoichiometry of the parent layered double hydroxide.

(iii) A comparison of the crystal structures of related salts is useful in interpreting the powder X-ray diffraction data as well as confirming the nature of the reactions which occur in the gallery region.

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