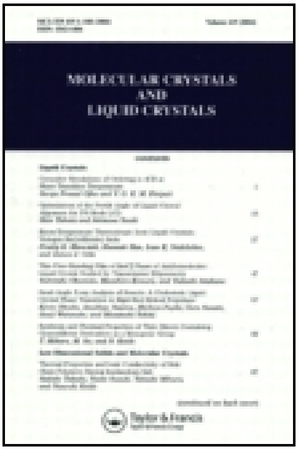
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 18 February 2013, At: 13:30
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Structural Characterisation of LDH-Organic Intercalates

Winnie Kagunya [a] , Malama Chibwe [a] & William Jones [a]

[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

Version of record first published: 23 Oct 2006.

To cite this article: Winnie Kagunya , Malama Chibwe & William Jones (1994): Synthesis and Structural Characterisation of LDH-Organic Intercalates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 155-160

To link to this article: http://dx.doi.org/10.1080/10587259408050097

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 155–160
Reprints available directly from the publisher
Photocopying permitted by license only
© 1994 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:30 18 February 2013

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF LDH-ORGANIC INTERCALATES

WINNIE KAGUNYA, MALAMA CHIBWE AND WILLIAM JONES*
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Abstract A range of layered double hydroxide-organic intercalation compounds have been prepared and characterised using powder XRD and IR spectroscopy. Two procedures have been used to prepare the intercalates. The first is by the conventional co-precipitation direct synthesis method. The other involves the so-called rehydration route. In most cases comparable results are obtained by both methods. Depending upon the nature of the anion both monolayer and bilayer guest arrangements seem possible.

INTRODUCTION

There is currently much interest in the synthesis and application of layered double hydroxides (LDHs) and in particular in procedures for incorporating large anionic species into the gallery regions of such host matrices.[1,2] The layer charge carried by LDHs, however, is significantly larger than that found in clays - particularly those clays with catalytic potential.[3] Several approaches to anion-incorporation in such high charge materials have, therefore, been reported, including various anion exchange processes, direct synthesis (co-precipitation) and rehydration after calcination.[4-9] Both organic and inorganic guests have been incorporated.

We describe here the synthesis of a range of aromatic organic intercalates (benzoate, terephthalate, p-toluene-sulphonate, trans-cinnamate, 1-naphthoate-carboxylate and 9-anthracene carboxylate) and compare the properties of these

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:30 18 February 2013

materials as a function of the method of preparation. Two methods of synthesis are used. The first is by co-precipitation (CP) and the second by rehydration of a previously calcined host (RM). We begin by comparing RM and CP as general strategies for preparing organic intercalates and then discuss specifically the role of the RM method as a general synthetic procedure.

EXPERIMENTAL

We have used a magnesium-aluminium carbonate LDH (Mg:Al ratio of 2:1) as the parent material for the present study. The respective intercalates will be designated as MGBE (benzoate), MGTE (terephthalate), MGPT (p-toluene-sulphonate), MGCN (trans-cinnamate), MGNA (1-naphthoate-carboxylate) and MGAT (9-anthracene carboxylate).

(i) Synthesis via the co-precipitation method (CP).[4,5]
Typically, an organic solution was prepared by mixing 0.1 moles of organic acid and 0.2 moles of NaOH in 200 ml of deionized water. Into this was added, over a one hour period and with extensive nitrogen purging and vigorous stirring, a solution containing 0.2 moles of $Mg(NO_3)_2.6H_2O$ and 0.1 moles of $Al(NO_3)_3.9H_2O$ in 160 ml water. The resulting gel was then aged at 75 ± 2 °C for 18 hours, cooled and filtered. The material was dried at 105 °C for 18 hours and then analysed.

(ii) Synthesis via the rehydration method (RM).[2]
0.1 moles of the organic acid and a stoichiometric amount of sodium hydroxide were added to 100 ml of water at 68 ± 3 °C, purged with nitrogen and refluxed for 25 minutes. The pH values of the various solutions were observed to lie between 10 and 11.5. The pH of the solution was then slowly lowered to 4.5 by the addition of the corresponding acid. After maintaining this pH for 25 minutes, 1 g of MgAl carbonate LDH which had been calcined at 550 °C for 18 hours was added. The mixture was stirred for 25 minutes and then filtered, washed under N_2 with hot water, and dried in an evacuated desiccator overnight. In the synthesis of the MgAl LDH intercalated with 9-anthracene carboxylate anions, washing of the LDH with acetone was necessary before drying to remove the carboxylic acid which had been adsorbed on the surface.

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:30 18 February 2013

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns (CuK$_\alpha$ radiation) for MGBE obtained *via* the RM and CP methods are shown in Fig. 1. The patterns are characteristic of an intercalated LDH although there are significant differences in the interlayer spacing and the peak widths, with the reflections of the CP product being narrower than those of RM. Indexing of the patterns confirms that each contain only a single phase. The d-spacing for the lowest (00ℓ) reflections are 16.33 and 7.74 Å for RM and CP respectively, which assuming the thickness of the cationic layers in the LDHs to be similar to that of brucite (4.8 Å), results in gallery heights of 11.53 and 2.94 Å for the RM and CP products respectively. The largest dimension of the benzoate anion is approximately 8.6 Å i.e. ca. 25 % less than the gallery height of the product prepared *via* RM. The value associated with the CP route probably indicates carbonate or hydroxide rather than benzoate anion incorporation.

The X-ray diffraction patterns for the terephthalate intercalates are shown in Fig. 2. The patterns may be indexed on the basis of a unit cell of dimensions *a* and *c* of 3.04 and 14.69 Å, and 3.05 and 14.41 Å for RM and CP products respectively. Such interlayer values are consistent with a theoretical d-spacing value of 14.6 Å for an LDH intercalated with terephthalate anions oriented close to perpendicular to the cationic layers.[5,10]

The diffractograms for MGAT and MGNA intercalates prepared using RM index to a repeat distance of 21.64 and 20.43 Å respectively. With a single row of anions perpendicular to the cationic layers an interlayer spacing similar to that for a benzoate anion intercalate (i.e. 13.4 Å) would be expected. The actual values suggest, however, that bilayer-like arrangements of 9-anthracene carboxylate and 1-naphthoate carboxylate anions may in fact be present within the galleries. The possibility of anions intercalating so as to form bilayers is supported by work on single-crystal data on pure sodium salts of chloro-cinnamate anions.[11] Such an arrangement allows a favourable electrostatic interaction of the carboxylic group with the cationic layer and a van der Waal interaction between the hydrocarbon part of the guest molecules. The XRD patterns for MGAT and MGNA indicate, however, that additional phases are present. It is not clear at this stage whether this is the result of hydroxide or carbonate intercalation or perhaps the organic molecule lying parallel to the LDH sheets. All three possibilities would result in similar d-spacings.

Diffraction patterns characteristic of an intercalated material are also observed for MGCN and MGPT prepared *via* RM. The repeat distances are 19.86 Å for MGCN and 18.84 Å for MGPT. These should be compared to the calculated values of 15.7 and 14.8 Å respectively based on simple geometrical models. The differences in the observed and expected interlayer spacings suggest that p-toluene sulphonate and trans-cinnamate anions are not arranged as a single row between the cationic sheets. The pattern for MGPT suggests that an additional phase (possibly formed by the intercalation of either carbonate or hydroxide anions in the galleries or the p-toluene sulphonate anions oriented parallel to the cationic layers) is also present.

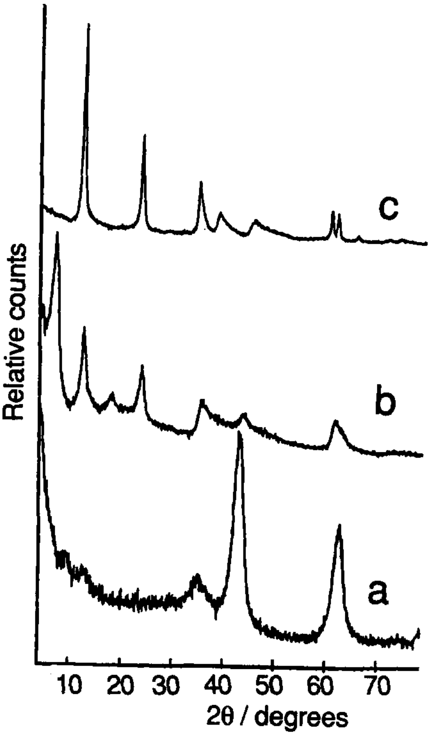


Fig. 1. Powder X-ray diffraction patterns of (a) MgAl LDH after calcination, (b) MGBE via RM and (c) MGBE via CP

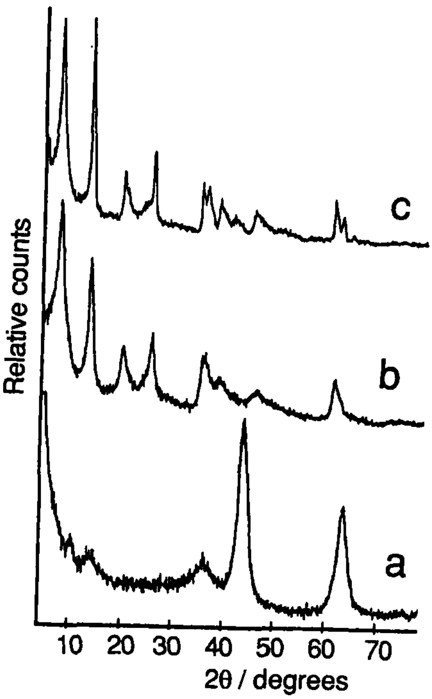


Fig. 2. Powder X-ray diffraction patterns of (a) MgAl LDH after calcination b) MGTE via RM and (c) MGTE via CP

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:30 18 February 2013

Infra-red spectroscopy confirms that the incorporation of organic guest is possible by both routes. Fig. 3 shows the infrared spectra of the parent LDH before and after calcination to the precursor. The spectra indicate some residual carbonate in the precursor.[12] The infrared spectra of MGCN prepared *via* RM is shown in Fig. 4. The relatively broad bands are likely to be the result of the overlap of peaks due to 'free' and intermolecular hydrogen bonded vibrations of the O-H groups. Hydrogen bonding is expected between the interlayer water and the structural hydroxide groups as well as with the guest anions.

There is some evidence from IR that acid molecules may be present in the interlayer region. These may be due to two factors. The carboxylic acid molecules may be intercalated along with the carboxylate anions (as has been observed in studies of the structure and dynamics of LDHs intercalated with fatty acids)[13]. Alternatively, some of the carboxylate anions may be strongly bonded to the hydroxide groups in the cationic layers such that they exhibit vibrations as though they were in the neutral acid form.

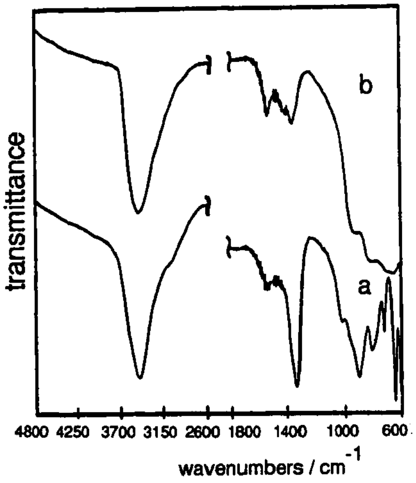


Fig. 3. IR of (a) MgAl LDH with carbonate as the charge-balancing anion and (b) after calcination to give the RM precursor.

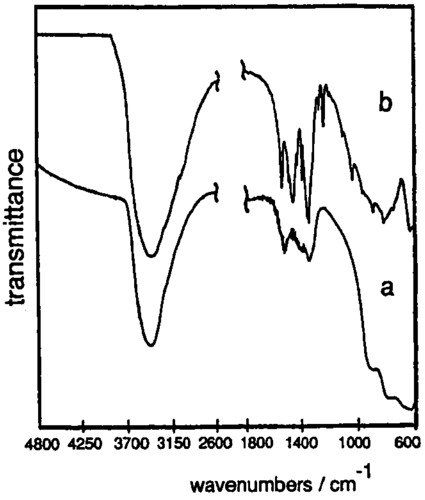


Fig. 4. IR spectra of (a) the precursor for RM synthesis and (b) product following exposure to a solution of sodium cinnamate

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:30 18 February 2013

DISCUSSION

An aim of this study has been to further investigate the rehydration route as a means of incorporating organic anions and to investigate whether there is any significant difference between the properties of the materials so produced and those made by direct synthesis. For most guest species comparable XRD and IR results are obtained. Where there are differences it is likely that slight variation in preparation procedure will allow for improved synthesis. There is evidence that neutral organic molecules may be introduced during synthesis.

A variety of structural patterns may be adopted by the guest within the interlayer region - either as a monolayer or in some instances bilayers. Further details concerning possible models will be presented elsewhere and methods for improving the crystallographic order of such intercalates will be described. The use of glycerol in assisting the incorporation of guests via the rehydration route has already been shown to influence the quality of the product *via* RM.[14]

REFERENCES

1 F. Cavani, F. Trifiro, and A. Vaccari, Catalysis Today, 11, 173 (1991).

2. M. Chibwe and W. Jones, in Pillared Layered Solids, Ed I. V. Mitchell (Elsevier, London) pp 67 (1990).

3. T. Kwon and T. J. Pinnavaia, Chem. Mater., 1, 381 (1989).

4. W. T. Reichle, CHEMTECH, 58 (1986).

5. M. A. Dredzon, Inorg. Chem., 27, 4628 (1988).

6. J. Wang, Y. Tain, R-C. Wang, J. L. Colon and A. Clearfield, in Synthesis/Characterisation and Novel Applications of Molecular Sieve Materials, Eds. R. L. Bedard *et al.* (MRS, Pittsburgh) 233, 63 (1991).

7. K. Chibwe and W. Jones, J. Chem. Soc., Chem. Commun., 926 (1989).

8. K. Chibwe and W. Jones, Chem. of Materials, 14, 926 (1989).

9. E. Narita, P. Kaviratna and T. J. Pinnavaia, Catalysis Letts., 805 (1991).

10. J. King and W. Jones, Mol. Cryst. Liq. Cryst., 211, 257 (1992).

11. J. Valim, B. M. Kariuki, J. King and W. Jones, Mol. Cryst. Liq. Cryst., 211, 271 (1992).

12. L. Pesic, S. Salipurovic, V. Marcovich, D. Vucelic, W. Kagunya and W. Jones, J. Mater. Chem. 2,, 1069 (1992).

13. M. Borja and P. K. Dutta, J. Phys. Chem., 96, 5434 (1992).

14 E. D. Dimotakis and T. J. Pinnavaia, Inorganic Chem., 29, 2393 (1990).

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:30 18 February 2013