

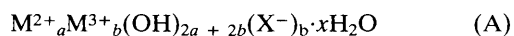
Intercalation of Organic and Inorganic Anions into Layered Double Hydroxides

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A procedure for intercalating layered double hydroxides is described: power X-ray diffraction, i.r., and thermogravimmetric measurements confirm that for sebacic acid, toluene-*p*-sulphonic acid, and dodecyl sulphate intercalation takes place and results in gallery heights of 11.5, 12.2, and 8.4 Å respectively.

Layered double hydroxides (LDHs, or the so-called anionic clays) are an important class of materials currently receiving considerable attention.¹⁻⁶ They consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules.^{1,2,7,8,9} In terms of charge they are mirror-images of the much studied family of cationic clay minerals.² They are represented by the general formula (A); where M²⁺ may be Mg, Ni, Co, Zn, or Cu and M³⁺ may be Al, Cr, or Fe. M²⁺/M³⁺ ratios between 1 and 5 are possible.



Cl⁻, OH⁻, and CO₃²⁻ are frequently cited as the charge-balancing anions although recent attempts have aimed at incorporating other guests, *e.g.* [V₁₀O₂₈]⁶⁻, see refs. 3 and 6. However, the direct synthesis of materials with anions other than carbonate is quite cumbersome and limited, requiring the total exclusion of carbon dioxide at each stage.^{4,10} Although the replacement of carbonate after synthesis is possible¹¹ this is frequently unsatisfactory because of the tenacity with which the carbonate anion is held.

Certain α,ω -dicarboxylic acid dianions may also be incorporated into the gallery region¹² although their incorporation does not take place readily (compare with sheet silicates¹³). Here we report a novel and versatile route for intercalating organic and inorganic anions by demonstrating that the exposure of heat-treated LDHs to the appropriate anion solution affords a facile preparative procedure for intercalation. Some of these anions have not been incorporated by other routes.

The method of synthesis of the LDH followed closely that of Reichle.⁴ The LDH was then calcined in air at 450 ± 10 °C for 18 h. 1 g of the calcined material was then added to a 0.05–0.1 M solution of the anion of interest in about 100 ml of decarbonated distilled water at 100 °C for 40 min. The product was separated by centrifuging and washed with hot distilled water. Once incorporated the organic-LDH appears stable.

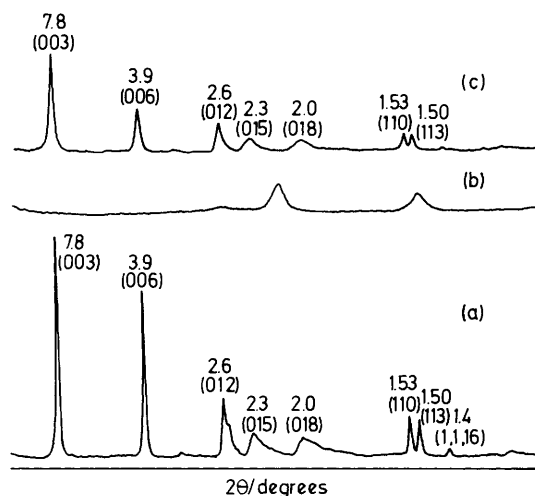


Figure 1. X-ray powder diffraction patterns of (a) Mg–Al–carbonate LDH as prepared, (b) after heat-treating at 450 °C for 18 h, and (c) after rehydrating (b) in 0.05 M sodium carbonate solution at room temperature. *d*-Spacing (Å) and Miller indices are shown.

Samples were examined by powder X-ray diffraction (x.r.d.), Fourier-transform i.r., thermogravimmetric analysis (t.g.a.), and atomic absorption spectroscopy. A typical composition for the starting LDH was Mg₆Al_{3.4}(OH)_{18.8}(CO₃)_{1.7}·4H₂O.

Specific anions used for intercalation include (i) dodecyl sulphate (in the form of sodium salt, C₁₂H₂₅OSO₃Na), (ii) sebacic acid (C₁₀H₁₈O₄), (iii) *p*-(SO₃)₆H₄Me, (iv) Fe(CN)₆³⁻, and (v) Cr₂O₇²⁻ (the last two as potassium salts).

The changes that accompany the heat-treatment of LDHs are well documented.^{4,14} Up to 500 °C weight-loss occurs in two stages: the first is associated with loss of interlayer water (until 300 °C) and thereafter decomposition of the carbonate

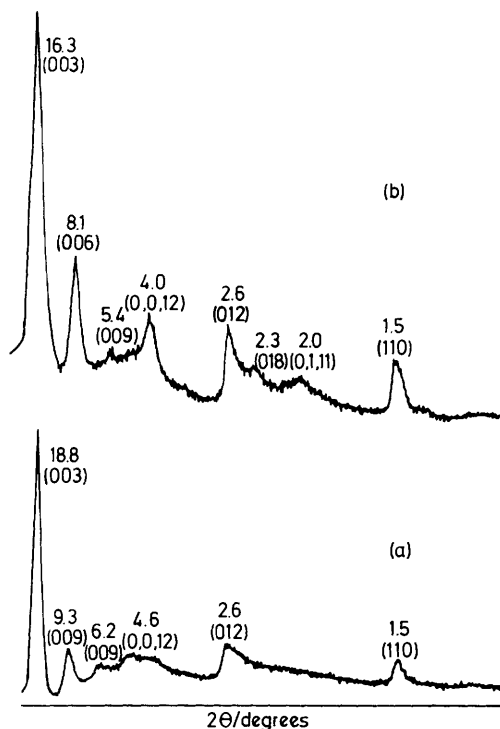


Figure 2. X-Ray powder diffraction patterns of (a) Ni-Al-sebacic acid intercalated by direct preparation and (b) rehydrated Mg-Al LDH in 0.05 M sebacic acid solution at 100 °C. d -spacing (Å) and Miller indices are shown.

anion and partial dehydroxylation occur. The accompanying changes in the X-ray pattern show that a poorly crystalline magnesium oxide-like solid results of composition $Mg_6Al_{3.3}O_{9.3}(OH)_{3.3}$.⁴ Figures 1(a) and (b) show the corresponding X-ray patterns. Exposure of this calcined material to carbonated water regenerates¹⁵⁻¹⁷ the starting LDH, Figure 1(c).

In the presence of sebacic acid (0.05 M aqueous solution) the original LDH is again observed to be reconstituted, although now in an expanded form, with the d_{003} reflection shifting from 7.8 to 16.3 Å. Given that the approximate thickness of the brucite layer is 4.8 Å the interlayer height generated is close to 11.5 Å suggesting that the anion is lying at an angle of about 35° to the layers, a phenomenon well known in clay intercalates.¹³ The direct synthesis of the sebacate intercalate^{4,12} gave a corresponding spacing of 18.8 Å, see Figure 2. I.r. spectroscopy confirms that no carbonate uptake has taken place. The elemental composition for this material was determined as $Mg_6Al_{3.3}(OH)_{18.6}(C_{10}H_{16}O_4)_{1.65}$ and is in complete agreement with the absence of any other interlayer anions other than sebacate. T.g.a. indicates that weight loss is

a two-stage process: 16% below 160 °C (attributed to interlayer and surface adsorbed water) and ca. 50% from 250 to 500 °C (attributed to dehydroxylation and loss of the sebacate dianion).

In the case of the dodecyl sulphate anion, under similar conditions, a mixed phase results, a spacing of 13.2 Å arising from the intercalated material whilst a value of 7.8 Å is suggestive of some carbonate form being present. The presence of the carbonate anion has been confirmed by i.r. spectroscopy. The degree of adsorption of monovalent anions is known to be less than that exhibited by higher charged species.¹⁶ A similar result was obtained for the p -(SO₃)C₆H₄-Me anion, yielding a d_{003} spacing of 17.0 Å in addition to a set of reflections due to carbonate intercalated species. The observed d value agrees quite well with Drezdson's value⁶ of 17.2 Å for a directly synthesized material for which it was proposed that the toluene- p -sulphonate is orientated with the aromatic ring perpendicular to the brucite layers.

Layer separations observed for ferricyanide, $Fe(CN)_6^{3-}$, and dichromate, $Cr_2O_7^{2-}$, were 6.0 and 5.2 Å respectively. Of the two, only the dichromate-intercalated product showed no carbonate interference. For the ferricyanide anion a similar layer separation was observed by Miyata *et al.*¹² who synthesized the material conventionally. The guest species is oriented with its C_2 axis perpendicular to the brucite layers.

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