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# Intercalation chemistry of layered double hydroxides: recent developments and applications†

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**Layered double hydroxides (LDHs) have been investigated for many years as host materials for a range of anion exchange intercalation reactions. In this role they have been used extensively as ion-exchange materials, catalysts, sorbents and halogen absorbers. More recently, there have been a tremendous number of new developments using these materials to store and deliver biologically active materials *in vivo*. Significant advances have been made recently on the characterisation of these materials, including structural studies and on the mechanism of intercalation using *in situ* techniques.**

## Introduction

Layered Double Hydroxides (LDHs) were discovered in the mid-19th Century. The first material discovered was hydrotalcite which subsequently gave its name to the large mineral group of naturally occurring LDHs. Hydrotalcite was discovered in 1842 in Sweden but the first exact formula, $[Mg_6Al_2(OH)_{16}]CO_3\cdot 4H_2O$ was not published until 1915 by Manasse.[1] Interest in LDH chemistry increased in 1942 following the publication of a series of papers by Feitknecht on what he called doppelschichtstrukturen (double sheet structures).[2] These compounds were assigned a structure which was made up of layers of one metal hydroxide intercalated with a layer of the second metal hydroxide. This structure type was disproved by Allmann and Taylor who carried out single crystal X-ray diffraction and found that both cations were actually in the same layer.[3,4]

Naturally occurring LDHs can be found in two polymorphic forms, namely rhombohedral and hexagonal (Fig. 1).[5]

In the rhombohedral form the lattice parameter, $c$, is equal to three times the interlayer separation, while in the hexagonal form $c$ is equal to twice the interlayer separation. Most naturally occurring crystals are of rhombohedral symmetry, however crystals containing both symmetry types have been discovered. For example, naturally occurring pyroaurite crystals $[Mg_6Fe_2(OH)_6](CO_3)\cdot 4H_2O$ consist of an inner core of hexagonal sjögrenite surrounded by an outer shell of rhombohedral pyroaurite. Today a range of synthetic LDHs can be prepared as a single pure phase.

## Chemical composition and structure

The chemical composition of an LDH is often described by the generic formula, $[M^{z+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{\zeta+}(X^{n-}{}_{\zeta/n})\cdot mH_2O$. Usually $z = 2$ with $M^{2+} = Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Co^{2+}$ or $Fe^{2+}$ and with $M^{3+} = Al^{3+}$, $Cr^{3+}$, $Mn^{3+}$, $Fe^{3+}$, $Ga^{3+}$, $Co^{3+}$ or $Ni^{3+}$ so that $\zeta = x$; In one case $z = 1$ with $M^+ = Li^+$ and $M^{3+} = Al^{3+}$ giving $\zeta = 2x - 1$. The values of $x$ have been reported to fall in the range $0.1 \leqslant x \leqslant 0.5$, however pure phases only exist for $0.2 \leqslant x \leqslant 0.33$.[6] For $x$ values not in this range compounds with different structures are obtained.[7,8] Brindley and Kikkawa proposed that for [Mg-Al] LDHs high values of $x$ lead to the formation of $Al(OH)_3$ owing to the increased number of aluminium octahedra and similarly low values of $x$ lead to the precipitation of $Mg(OH)_2$ owing to a high density of Mg containing octahedra in the sheets.[9] LDHs containing two different $M^{3+}$ or $M^{2+}$ cations have also been synthesised.[10–14] Table 1 summarises some of the commonly found LDHs. LDHs are made of layers of metal cations ($M^{2+}$ and $M^{3+}$) of similar ionic radii, which are coordinated by six oxygen atoms forming $M^{2+}/M^{3+}(OH)_6$ octahedra. These octahedra form two-dimensional sheets *via* edge sharing and may stack together by hydrogen bonding between the hydroxyl groups of adjacent sheets.

Substituting $M^{3+}$ cations of a similar ionic radius to $Mg^{2+}$, *e.g.* $Al^{3+}$, into $Mg(OH)_2$ produces a positively charged framework, therefore anions must intercalate between adjacent layers in order to maintain charge neutrality.[82] Ions such as $Be^{2+}$ are too small for octahedral coordination in the layers and ions of comparable size to $Ba^{2+}$ are too large.[18,83] All dipositive metal ions from $Mg^{2+}$ to $Mn^{2+}$ except $Cu^{2+}$ form hydrotalcites. $Cu^{2+}$ only forms hydrotalcites in the presence of other metal dications owing to the Jahn–Teller effect. The Jahn–Teller effect leads to the formation of the more

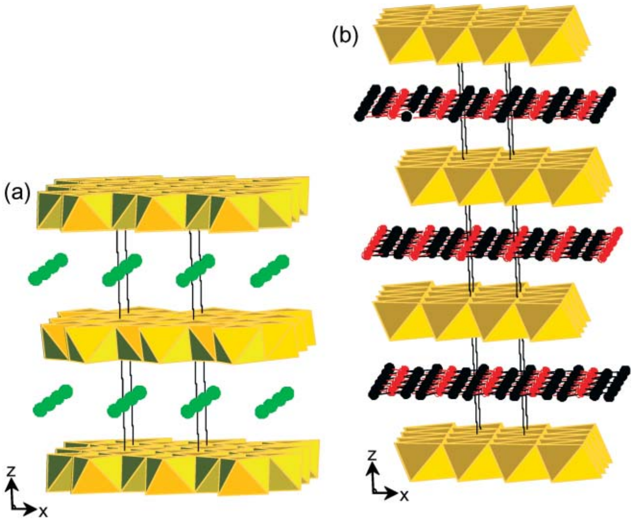

**Fig. 1** General structure of an LDH showing the polymorphic stacking patterns: (a) hexagonal, (b) rhomohedral.

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**Table 1** Summary of the commonly reported LDHs

| $M^{2+}$ | $M^{3+}$ | Interlayer anion | Chemical composition | References |
|---|---|---|---|---|
| Ca | Al | $CO_3$ | $[Ca_{0.66}Al_{0.33}(OH)_2](CO_3)_{0.17}\cdot nH_2O$ | 15 |
| Ca | Al | $NO_3$ | $[Ca_{0.66}Al_{0.33}(OH)_2](NO_3)_{0.33}\cdot 0.66H_2O$ | 16, 17 |
| Ca | Al | OH | $[Ca_{0.66}Al_{0.33}(OH)_2](OH)_{0.33}\cdot nH_2O$ | 15 |
| Cd | Al | $CO_3$ | $[Cd_{0.67}Al_{0.33}(OH)_{1.67}](CO_3)_{0.33}\cdot 0.5H_2O$ | 18, 19 |
| Cd | Al | $NO_3$ | $[Cd_{0.67}Al_{0.33}(OH)_{1.67}](NO_3)_{0.67}\cdot 0.5H_2O$ | 19 |
| Co | Al | Cl | $[Co_{0.66}Al_{0.33}(OH)_2]Cl_{0.33}\cdot nH_2O$ | 20, 21 |
| Co | Al | OH | $[Co_{0.75}Al_{0.25}(OH)_2](OH)_{0.13}\cdot nH_2O$ | 15 |
| Cu | Al | $[Fe(CN)_6]$ | $[Cu_{0.88}Al_{0.5}(OH)_2][Fe(CN)_6]_{0.31}\cdot 1.25H_2O$ | 15, 22 |
| Cu | Cr | $C_6H_4$-1,4-$(CO_2)_2$ | $[Cu_{0.6}Cr_{0.4}(OH)_2][C_6H_4\text{-1,4-}(CO_2)_2]_{0.2}\cdot 0.6H_2O$ | 2, 22 |
| Cu | Cr | Cl | $[Cu_{0.69}Cr_{0.31}(OH)_2]Cl_{0.31}\cdot 0.61H_2O$ | 15, 23, 24 |
| Cu | Cr | Dodecyl-sulfate | $[Cu_{0.66}Cr_{0.33}(OH)_2](\text{dodecylsulfate})_{0.33}\cdot nH_2O$ | 15 |
| Li | Al | Br | $[Li_{0.33}Al_{0.66}(OH)_2]Br_{0.33}\cdot nH_2O$ | 25, 26 |
| Li | Al | Cl | $[Li_{0.33}Al_{0.66}(OH)_2]Cl_{0.33}\cdot nH_2O$ | 25, 27–36 |
| Li | Al | Cl (rhomb) | $[Li_{0.33}Al_{0.66}(OH)_2]Cl_{0.33}\cdot nH_2O$ | 37 |
| Li | Al | $CO_3$ | $[Li_{0.33}Al_{0.66}(OH)_2](CO_3)_{0.16}\cdot nH_2O$ | 28, 38 |
| Li | Al | $NO_3$ | $[Li_{0.33}Al_{0.66}(OH)_2](NO_3)_{0.33}\cdot nH_2O$ | 16, 25, 26, 33 |
| Li | Al | OH | $[Li_{0.33}Al_{0.66}(OH)_2](OH)_{0.33}\cdot nH_2O$ | 26 |
| Li | Al | $SiO(OH)_3$ | $[Li_{0.33}Al_{0.66}(OH)_2][(OH)_3SiO]_{0.33}\cdot nH_2O$ | 36 |
| Li | Al | $SO_4$ | $[Li_{0.33}Al_{0.66}(OH)_2](SO_4)_{0.17}\cdot nH_2O$ | 26 |
| Mg | Al | Cl | $[Mg_{0.66}Al_{0.33}(OH)_2]Cl_{0.33}\cdot nH_2O$ | 20, 21, 27, 36, 39–43 |
| Mg | Al | $ClO_4$ | $[Mg_{0.75}Al_{0.25}(OH)_2](ClO_4)_{0.18}(CO_3)_{0.018}\cdot 0.46H_2O$ | 9, 44 |
| Mg | Al | $CO_3$ | $[Mg_{0.66}Al_{0.33}(OH)_2](CO_3)_{0.17}\cdot nH_2O$ | 9, 15, 39, 45–53 |
| Mg | Al | $Fe(CN)_6$ | $[Mg_{0.741}Al_{0.259}(OH)_2][Fe(CN)_6]_{0.067}(CO_3)_{0.002}\cdot 1.05H_2O$ | 20, 46 |
| Mg | Al | $NO_3$ | $[Mg_{0.66}Al_{0.33}(OH)_2](NO_3)_{0.33}\cdot nH_2O$ | 16, 54–60 |
| Mg | Al | $SiO(OH)_3$ | $[Mg_{0.75}Al_{0.25}(OH)_2][(OH)_3SiO]_{0.25}\cdot nH_2O$ | 36 |
| Mg | Cr | $CO_3$ | $[Mg_{0.71}Cr_{0.29}(OH)_2](CO_3)_{0.145}\cdot 0.5H_2O$ | 61 |
| Mg | Cr | $Fe(CN)_6$ | $[Mg_{0.56}Cr_{0.44}(OH)_2][Fe(CN)_6]_{0.15}\cdot 0.7H_2O$ | 61 |
| Mg | Cr | Oxalate | $[Mg_{0.61}Cr_{0.39}(OH)_2](C_2O_4)_{0.0975}\cdot 0.5H_2O$ | 61 |
| Mg | Fe | $CO_3$ | $[Mg_{0.75}Fe_{0.25}(OH)_2](CO_3)_{0.125}\cdot 0.5H_2O$ | 62, 63 |
| Mg | Al, Fe | $CO_3$ | $[Mg_{0.74}Fe_{0.11}Al_{0.15}(OH)_2](CO_3)_{0.13}\cdot 0.70H_2O$ | 11 |
| Mg, Pd | Al | $CO_3$ | Atomic Ratios 66 : 5 : 29 | 10 |
| Mg, Pt | Al | $CO_3$ | Atomic Ratios 67 : 4 : 29 | 10 |
| Mg | Al, Rh | $CO_3$ | Atomic Ratios 71 : 24 : 5 | 10 |
| Mg | Al, Ir | $CO_3$ | Atomic Ratios 71 : 24 : 5 | 10 |
| Mg | Al, Ru | $CO_3$ | Atomic Ratios 71 : 24 : 5 | 10 |
| Mg | Al, Zr | $CO_3$ | Atomic Ratios 3 : 0.52 : 0.50 | 64 |
| Mg | V | $CO_3$ | $[Mg_{0.52}V_{0.48}(OH)_2](CO_3)_{0.24}\cdot 0.86H_2O$ | 12, 65 |
| Mn | Al | Cl | $[Mn_{0.66}Al_{0.33}(OH)_2]Cl_{0.33}\cdot nH_2O$ | 20, 66 |
| Ni | Al | Cl | $[Ni_{0.75}Al_{0.25}(OH)_2]Cl_{0.25}\cdot nH_2O$ | 20, 67, 68 |
| Ni | Al | $CO_3$ | $[Ni_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.125}\cdot nH_2O$ | 18, 63 |
| Ni | Al | $NO_3$ | $[Ni_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.20}(CO_3)_{0.066}\cdot 0.7H_2O$ | 67 |
| Ni | Co | $CO_3$ | $[Ni_{0.75}Co_{0.25}(OH)_2](CO_3)_{0.125}\cdot 0.38H_2O$ | 13 |
| Ni | Fe | $CO_3$ | $[Ni_{0.75}Fe_{0.25}(OH)_2](CO_3)_{0.125}\cdot 0.38H_2O$ | 13, 63 |
| Ni | Fe | $SO_4$ | $[Ni_{0.7}Fe_{0.3}(OH)_2](SO_4)_{0.17}\cdot nH_2O$ | 15 |
| Ni | V | $CO_3$ | $[Ni_{0.82}V_{0.18}(OH)_2](CO_3)_{0.09}\cdot 0.96H_2O$ | 69 |
| Ni, Cu | Al | $CO_3$ | $[Ni_{0.30}Cu_{0.38}Al_{0.32}(OH)_2](CO_3)_{0.16}\cdot 1.23H_2O$ | 70 |
| Zn | Al | Cl | $[Zn_{0.66}Al_{0.33}(OH)_2]Cl_{0.33}\cdot 0.66H_2O$ | 15, 20, 21, 23, 42, 43, 71–77 |
| Zn | Al | $CO_3$ | $[Zn_{0.75}Al_{0.25}(OH)_2](CO_3)_{0.13}\cdot nH_2O$ | 15, 18, 78 |
| Zn | Al | $NO_3$ | $[Zn_{0.66}Al_{0.33}(OH)_2](NO_3)_{0.33}\cdot 0.66H_2O$ | 16 |
| Zn | Cr | Br | $[Zn_{0.66}Cr_{0.33}(OH)_2]Br_{0.33}\cdot 0.66H_2O$ | 79 |
| Zn | Cr | Cl | $[Zn_{0.66}Cr_{0.34}(OH)_2]Cl_{0.34}\cdot 0.71H_2O$ | 20, 21, 24, 42, 73, 79, 80 |
| Zn | Cr | $ClO_4$ | $[Zn_{0.66}Cr_{0.33}(OH)_2](ClO_4)_{0.33}\cdot 0.66H_2O$ | 79 |
| Zn | Cr | F | $[Zn_{0.66}Cr_{0.33}(OH)_2]F_{0.33}\cdot 0.66H_2O$ | 79 |
| Zn | Cr | $HPO_4$ | $[Zn_{0.66}Cr_{0.33}(OH)_2](HPO_4)_{0.17}\cdot 0.66H_2O$ | 79 |
| Zn | Cr | I | $[Zn_{0.66}Cr_{0.33}(OH)_2]I_{0.33}\cdot 0.66H_2O$ | 79 |
| Zn | Cr | $NO_3$ | $[Zn_{0.66}Cr_{0.33}(OH)_2](NO_3)_{0.33}\cdot 0.66H_2O$ | 16, 79–81 |
| Zn | Cr | $SO_4$ | $[Zn_{0.66}Cr_{0.33}(OH)_2](SO_4)_{0.17}\cdot 0.66H_2O$ | 79 |
| Zn | Cr | n-$C_aH_{2a+1}SO_4$ | $[Zn_{0.66}Cr_{0.33}(OH)_2](\text{n-}C_aH_{2a+1}SO_4)_{0.33}\cdot 0.66H_2O$ | 79 |

energetically favourable distorted octahedra when the ratio of $Cu^{2+}$ to the other dipositive metal ion is greater than 1.[24,70] All trivalent metal ions, except $Ti^{3+}$, owing to the instability of this oxidation state for Ti, form hydrotalcites. The formation in air of a LDH containing $V^{3+}$ was not reported until 1996 when Kooli *et al.* synthesised [Mg-V] and [Mg-V-Al] LDHs by the coprecipitation method and formed compounds such as $[Mg_{0.616}V_{0.383}(OH)_2](CO_3)_{0.191}\cdot 0.65H_2O$.[12] Labajos *et al.* also synthesised a LDH containing $Ni^{2+}$ and $V^{3+}$ with varying ratios of the two ions.[69]

When $z = 2$, the cations are not ordered in the octahedral sites, except in $[Ca_2Al(OH)_6]_2SO_4\cdot 6H_2O$ (Fig. 2a) where complete ordering is observed.[84] Ordering of the cations is also observed in the unique LDH which contains $Li^+$ ions in the metal layers ($z = 1$). $AlO_6$ octahedra are edge sharing as in gibbsite with lithium cations in 1/3 of the octahedral sites in the $Al(OH)_3$ layers (Fig. 2b).

Recently, Fogg *et al.* synthesised the rhombohedral form of [Li-Al] LDH using the bayerite polymorph of $Al(OH)_3$ rather than gibbsite which is used to synthesise the more common hexagonal [Li-Al] LDH. The rhombohedral LDH intercalated simple carboxylates but did not form staging compounds unlike the hexagonal form.[37]

The interlayer region also contains water molecules, the amount of water in the interlayer region is determined by factors such as the nature of the interlayer anions, the water vapour pressure and temperature.[9,85–88] The water molecules are connected to both the metal hydroxide layers and interlayer anions through extensive hydrogen bonding.[44,82,89] The concept that these hydrogen bonds are continuously breaking and

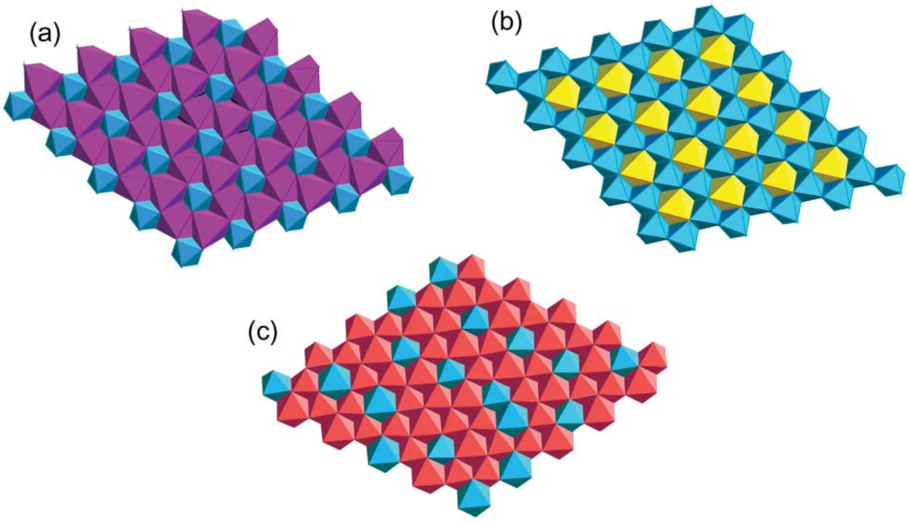


**Fig. 2** Structures of (a) $[Ca_2Al(OH)_6]_2SO_4\cdot6H_2O$, (b) $[LiAl_2(OH)_6]Cl$ and (c) $[Mg_{2.25}Al_{0.75}(OH)_6]OH$ LDHs in the *ab*-plane showing the arrangement of the metal cations.

reforming and that the water molecules are in a continuous state of flux is supported by NMR experiments. Hence the precise nature of the interlayer region is extremely complex.

## Intercalation chemistry

Intercalation reactions are particularly important as they can be utilised to dramatically change the chemical, electronic, optical, and magnetic properties of a host lattice. In addition, intercalation reactions can be used as a low temperature (*chimie douche*) method to prepare novel materials which may not be accessible by other techniques.

The intercalation chemistry of LDH hosts is very extensive. A huge variety of anions ($X^{n-}{}_{\zeta/n}$) can be incorporated into the interlayer region of these hosts using a range of methods. The dimensions and functional groups of the guest molecule are critical in determining the separation between the layers. The number (monolayer, bilayer), size, orientation of the guest as well as the interactions between the negatively charged guest and positively charged host are all critical factors.[90] Simple inorganic anions such as the halides, $OH^-$, $CO_3^{2-}$, $SO_4^{2-}$ and $ClO_3^-$ have all been incorporated.[28,86,91] The intercalation of silicate anions has also been achieved,[73,92,93] for example $SiO(OH)_3^-$ has been incorporated into [Mg-Al] and [Li-Al] LDHs as well as other hosts *via* the ion-exchange method. It is thought that the silicate anions condense into a 2D six ring structure between the LDH layers. Both XRD and infrared experiments suggest that the silicates anions form a puckered layer configuration.[36]

Phthalocyanines can also be incorporated into LDHs *via* the ion-exchange route. Carrado *et al.* intercalated copper(II) phthalocyanine and found that the guest was orientated parallel to the cationic hectorite clay layers and perpendicular to the anionic LDH clay layers in correlation with the layer charge density of the host.[94] In contrast Dutta and Puri intercalated the nickel phthalocyanine tetrasulfonate ion into [Li-Al] LDH and found that the intercalate exhibited a relatively small interlayer separation of 5.81 Å signifying that the phthalocyanine adopts a parallel orientation with respect to the layers.[29] A range of polyoxometalates have also been intercalated *via* the ion-exchange, coprecipitation and rehydration methods.[6,28,46,95–97] Chibwe and Jones intercalated $Cr_2O_7^{2-}$ by the rehydration of calcined [Mg-Al] layered double oxide (LDO) and obtained a product with a *d*-spacing of 5.2 Å.[46] Intercalation compounds of transition metal complexes have also been prepared. $Fe(CN)_6^{3/4-}$ has been intercalated into a variety of LDHs by the 3 common intercalation procedures giving rise to compounds such as $[Mg_{0.741}Al_{0.259}(OH)_2\{Fe^{II}(CN)_6\}_{0.067}(CO_3)_{0.002}\cdot1.05H_2O]$.[20,46] Carlino *et al.* also attempted the intercalation of the related $K_3Fe(C_2O_4)_3\cdot3H_2O$ into [Mg-Al] LDH of formula $[Mg_6Al_{3.4}(OH)_{18.82}](CO_3)_{1.51}(NO_3)_{0.36}\cdot4.5H_2O$ and discovered that only partial ion-exchange took place. The reaction products were found to be polyphasic owing to the presence of products with the complex on the surface of the individual crystallites and the fact that some of the host remained.[98] Keggin ions, for example $[H_2W_{12}O_{40}{}^{6-}]$, have also been intercalated into LDHs.[99] More recent advances are the synthesis of a new Ru containing LDH, the intercalation of Cu and Ni complexes and the synthesis of nanocomposites. Inacio *et al.* investigated the intercalation of the aquapentachlororuthenate(III) complex $[RuCl_5H_2O]^{2-}$ by ion-exchange into a variety of LDHs but found that exchange was complete only with [Zn-Al-Cl] LDH.[42] Copper and nickel nitrilotriacetate ($[Cu(nta)]^-$ and $[Ni(nta)]^-$) complexes have also been intercalated by both direct and indirect ion-exchange methods into [Zn-Cr] LDH.[81] In the case of $[Cu(nta)]^-$ a mixture of products with *d*-spacings of approx. 14.2 and 12.0 Å were formed at ambient temperature. However, at 60 °C only the product with the lower basal spacing formed. In contrast, for the Ni complex only the product with a *d*-spacing of 14.2 Å formed at 25 °C and the formation of the product with a *d*-spacing of 12.0 Å occurs only at temperatures of about 100 °C. These differences were explained to arise from the complexes being arranged in a tilted (12.0 Å) or vertical arrangement (14.2 Å) in the interlayer region with the five-membered rings parallel to the *c* direction in the vertical orientation and at an angle of 45° in the tilted orientation. The tilted orientation is energetically favoured owing to the fact that greater host–guest interactions (*i.e.* more hydrogen bonding) are possible but this orientation cannot be achieved at low temperatures.

The synthesis of LDH nanocomposites with polymeric guest molecules is difficult to achieve as the methods used for polymer incorporation into other layered materials are not successful for LDHs.[100] For example, exfoliation of LDH sheets does not take place easily owing to the high charge density of the layers. The synthesis and characterisation of polymer interleaved layered double hydroxides has recently been reviewed by Leroux and Besse.[15] These nanocomposite materials consist of the LDH sheets lying on top of each other with the interlayer space being filled by a polymer guest. Various anionic polymers can be inserted between the layers of a LDH. The incorporation can be carried out by *in situ* polymerisation of an intercalated monomer (Fig. 3a), or by

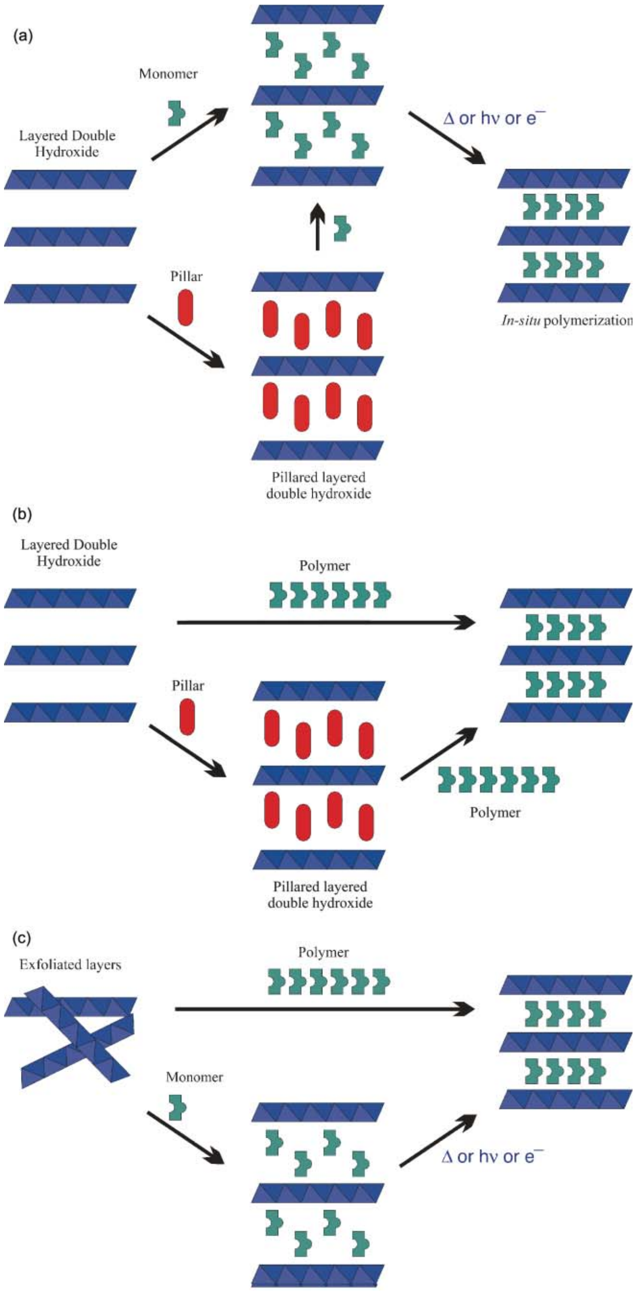


**Fig. 3** The synthesis of polymer intercalated LDHs: (a) *in situ* polymerisation of an intercalated monomer, (b) direct intercalation of a high molecular weight macromolecule, (c) restacking of the LDH layers over a polymer.

direct intercalation of a high molecular weight macromolecule (Fig. 3b) by ion-exchange or using the co-precipitation method to synthesise the host in the presence of the polymer. For example heating an acrylate [Mg-Al] LDH hybrid at 80 °C leads to polymerisation of the guest. Poly(α,β-aspartate) can be inserted into [Mg-Al] LDH by direct intercalation as a cosolute in a basic reaction. The restacking of layers over the polymer is also theoretically possible and has been attempted. However, it is very difficult owing to the fact that exfoliation of the layers is problematic. The incorporation of polymer chains *via* the reconstruction method has been more successful (Fig. 3c).

Challier and Slade also reported the *in situ* polymerisation of preintercalated aniline in [Cu-Cr] and [Cu-Al] LDHs, however these products were initially pillared by terephthalate and hexacyanoferrate(II) anions.[22] Analysis of the XRD patterns of the products confirmed the presence of multiple phases. Similarly the *in situ* polymerisation of pre-intercalated acetonitrile has been reported.[101] The direct synthesis approach has been used to intercalate poly(vinyl alcohol) into [Ca-Al] LDH leading to the formation of a well ordered layered nanocomposite.[102,103] Whilton also carried out the intercalation of aspartate monomers into [Mg-Al-$CO_3$] LDH, thermal polycondensation of the intercalate followed by base hydrolysis gave rise to poly(α,β-aspartate).[53] These nanocomposite materials may have many useful applications arising from the constraints placed on the guest, in addition the presence of the inorganic LDH component in the organic matrix should impart enhanced thermal and rheologic properties.

Attempts at synthesising homogeneous intercalates containing 2 different anionic species have also been undertaken.[13,80] Schoellhorn and Otto investigated the competition intercalation reaction of $ClO_4^-$ and $NO_3^-$ with varying ratios of the two anions into [Zn-Cr] LDH. The two phases were found to coexist over a very narrow range implying that the formation of phases with mixed anions in the interlayer region is energetically unfavourable and the activation energy required for the transition is large.

We are particularly interested in the intercalation of organic ions, the mechanisms and selectivities of these reactions. The various methods for the intercalation of a range of carboxylic acids into LDHs have been reviewed by Carlino.[45] Miyata and Kumura reported the first example of exchange of interlayer ions by organic anions upon intercalating a series of dicarboxylate anions with increasing number of carbon atoms into [Zn-Al] LDH. Measurement of the position of the (006) Bragg reflection in the powder X-ray pattern of the products revealed that the interlayer separation of the products increased linearly with increasing number of carbon atoms.[18] A similar trend was observed for the intercalation of alkyl sulfates into [Zn-Cr] chloride and nitrate LDHs where an increase in *d*-spacing was observed with increasing chain length.[79] Meyn *et al.* confirmed this relationship for aliphatic carboxylate anions and also carried out comprehensive studies on the intercalation of organic acids into a range of layered double hydroxides ([Zn-Cr], [Zn-Al], [Mg-Al], [Ca-Al] and [Li-Al] LDHs).[16] Fogg *et al.* also observed a linear increase in interlayer separation with the number of carbon atoms for the intercalation of a range of dicarboxylates into $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ (Fig. 4).[31]

The intercalation of benzoate and terephthalate has received particular attention owing to the different guest orientations under different conditions (vertical and horizontal).[6,22,29,43,52,59,60,95,104–108] It has been found that the orientation of both ions in the interlayer region of the LDH is determined by factors such as the charge of the layers and the amount of interlayer water present. Kooli *et al.* synthesised [Mg-Al] benzoate and terephthalate intercalates while varying the Mg : Al ratio between 1 and 5. Low Mg : Al ratios (*i.e.* high layer charge resulting in greater electrostatic repulsion between the positively charged layers) and high water content were found to favour the vertical orientation (monolayer for the

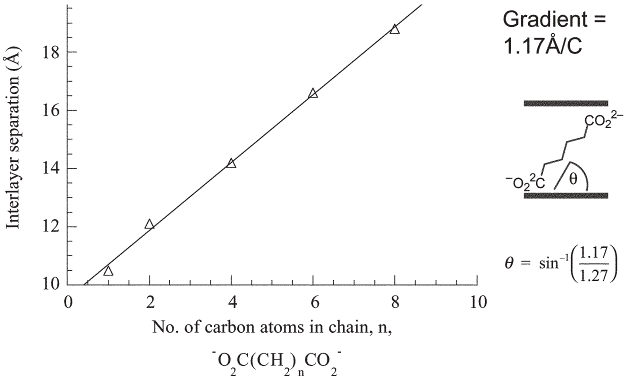


**Fig. 4** Plot of interlayer separation against the number of C atoms, *n*, in the chain of $^-O_2C(CH_2)_nCO_2^-$.

terephthalate intercalate and bilayer like structure for benzoate) of the guests in the interlayer region.[59]

Most recently the focus has shifted to the intercalation of biologically active materials such as porphyrins,[50,109,110] nucleoside phosphates,[57,58,68,111] drugs,[39,40,112–115] vitamins,[116] amino acids[53,117,118] and fatty acids.[16,27] The first layered double hydroxide–porphyrin intercalation compound was prepared by Park *et al.*[50] 5,10,15,20-Tetra(4-sulfanatophenyl)-porphyrin (TSPP) was intercalated into [Mg-Al] LDH. This was achieved by stirring a suspension of the host in a solution of $Na_4$TSPP at 60 °C for one week. The interlayer spacing of the intercalate was found to be 22.4 Å which indicates that the porphyrin intercalated with the molecular plane perpendicular to the hydroxide layers. Elemental analysis confirmed that 81% of the $Cl^-$ ions had been replaced and infrared spectroscopy was used to prove that the porphyrin intercalated intact.

Borja and Dutta investigated the intercalation reaction of long chain fatty acids of the type $CH_3(CH_2)_nCOOH$ where $n = 10,12,14$ into [Li-Al] and [Mg-Al] LDHs.[27] The carboxylic acid is ion-exchanged as a monolayer in the case of [Li-Al] LDH but for [Mg-Al] LDH it is intercalated as the acid form as a bilayer. The packing of the anions within the LDH layers was found to be influenced by the layer charge.

The intercalation of a variety of vitamins has also been carried out. Hwang *et al.*[116] intercalated Vitamin A (retinoic acid), Vitamin C (ascorbic acid) and Vitamin E (tocopherol) by the coprecipitation method into [Zn-Al] LDH. In solution these vitamins are normally all sensitive to light, heat and oxygen, it is thought that incorporating these molecules into a layered inorganic lattice may lead to stabilisation resulting in a wider range of potential applications. Vitamins C and E both form monolayers in the interlayer region whereas Vitamin A forms a bilayer with a gallery height of 33 Å.

Choy *et al.* intercalated large macro-biological molecules such as DNA, ATP and nucleosides into $[Mg_2Al(OH)_6]NO_3 \cdot 1.2H_2O$. Infrared spectroscopy has been used to confirm that the biomolecules maintained their integrity in the interlayer region. These reactions result in the synthesis of novel bioinorganic/inorganic nanohybrids with practical significance.[119,120] The authors are trying to exploit this approach to develop new DNA reservoirs or carriers for the delivery of genetic material to cells.[54] It is believed that the host lattice may protect these relatively delicate biomolecules from degradation and also aid their transport to specific targets within the body. For example, if deintercalation does not occur in the stomach or small intestine the hybrid may be transferred across the intestinal mucosa into the bloodstream. This neutral complex has the advantage that it does not suffer from repulsive interactions between the negatively charged cell membrane and the anionic bioactive molecules during transfer into mammalian cells *via* endocytosis.[121,122] Once inside the cells some of the LDH, which is unstable in acidic conditions, is dissolved by lysosomes resulting in the release of the intercalated molecule. In addition, the anions in the cell may partially replace the interlayer biomolecules so the encapsulated molecules can be released inside the cell *via* ion-exchange. Cellular uptake experiments have been performed in order to investigate the delivery potential of these hybrids. Choy *et al.* monitored the uptake of isotope labelled [$\gamma$-$^{32}$P]ATP-LDH by eukaryotic cells and found that the rate of uptake of the hybrid was much higher than the uptake of ATP alone owing to a reduction in electrostatic repulsion.[58]

Anionic drug molecules have also been intercalated into a variety of LDHs,[39,112,114,115] the aim being to determine the feasibility of using these intercalation compounds as materials for the storage, transport and ultimately controlled release of the drug. The release properties of the drugs have been investigated by adding their intercalation compounds to samples of simulated gastrointestinal and intestinal fluid (Fig. 5).

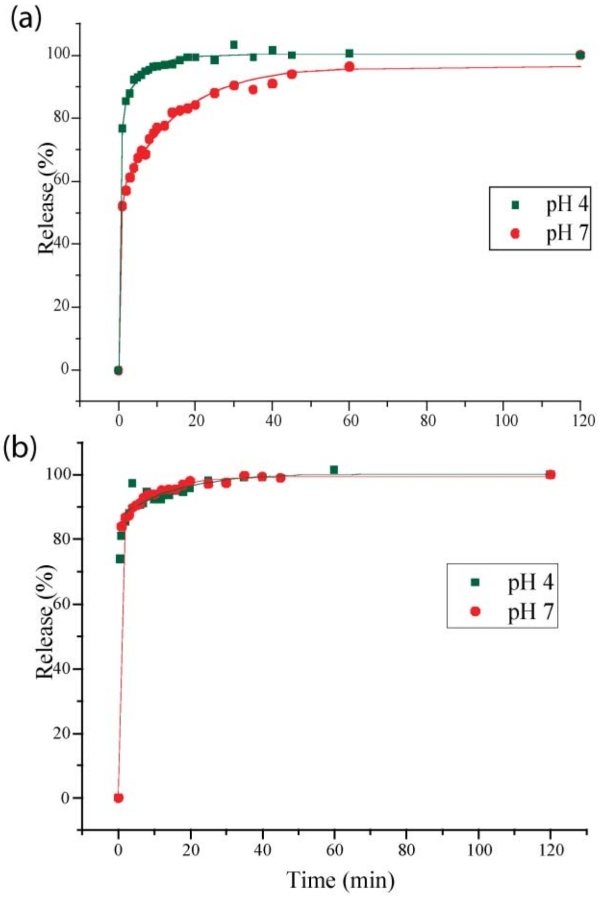
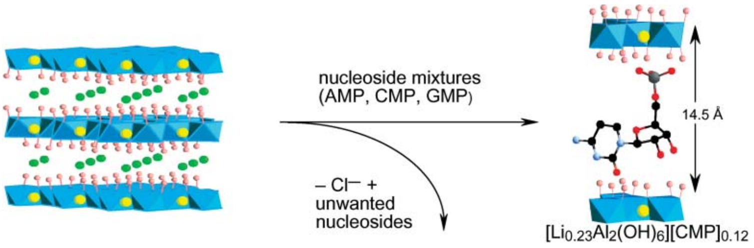


**Fig. 5** Release profiles for drug molecules from $[Li_xAl_2(OH)_6][drug]_x \cdot yH_2O$ LDHs: (a) release of diclofenac at pH 4 and pH 7 and (b) release of gemfibrozil at pH 4 and pH 7.

Owing to the instability of LDHs at low pH it was found that release of the drugs in simulated gastrointestinal fluid was instantaneous, however release in simulated intestinal fluid was found to be much slower. Therefore if the intercalation compound was encapsulated in an enteric coating thereby protecting it from the acidic conditions in the stomach, then these materials may be suitable for the controlled release of the drug in the small intestine.

## Selective intercalation chemistry

In most cases intercalation reactions are not selective processes, they are usually driven by either oxidation–reduction, ion-exchange, acid–base and donor–acceptor reactions. However certain layered double hydroxides exhibit shape selective intercalation reactions.[17,30–32,34,35,75,123] Furthermore, in some cases it is possible to control this shape selectivity by altering the temperature and the reaction solvent. An example is the intercalation of 1,5-naphthalenedisulfonate and 2,6-naphthalenedisulfonate into $[LiAl_2(OH)_6]Cl \cdot H_2O$. From an equimolar mixture of the 1,5 and 2,6 isomers at 100 °C it is found that the preference for the 1,5 over the 2,6 isomer is in excess of 98 : 2. However the preference for the 1,5 isomer decreases as the temperature is lowered, at 20 °C the ratio of the 1,5 *versus* the 2,6 intercalation product is 27 : 73 respectively. The crossover in preference from the 1,5 product at high temperature to the 2,6 at low temperatures is found to take place at 45 °C. The solvent used is also critical for determining the ratios of the two reaction products. In fact in a 50% acetonitrile : water mixture the 1,5 isomer does not predominate (only 40% is present) at 100 °C. The temperature dependence in the acetonitrile : water mixture is the reverse of that for pure water. It is thought that the solvent dependence



| Guest Anions<br>NMP1 : NMP2 | T (°C) | Selectivity Ratios<br>NMP1 : NMP2 |
|---|---|---|
| $Na_2CMP$ : $Na_2AMP$ | RT | No reaction |
| | 40 | No reaction |
| | 60 | 80.0 : 20.0 |
| | 80 | 80.5 : 19.5 |
| | 100 | 79.7 : 20.3 |
| $Na_2CMP$ : $Na_2GMP$ | RT | No reaction |
| | 40 | No reaction |
| | 60 | 72.4 : 27.6 |
| | 80 | 75.6 : 24.4 |
| | 100 | 73.7 : 26.3 |

**Fig. 6** Schematic representation of the intercalation of nucleosides in $[LiAl_2(OH)_6]Cl$ intercalate showing selective intercalation of $CMP^{2-}$ over $AMP^{2-}$ and $GMP^{2-}$.

arises from the different solvation enthalpies of the ions.[32] [Li-Al] LDH has also been found to preferentially intercalate certain pyridinecarboxylate and pyridinedicarboxylate isomers over others.[34,35] More recently the first example of selective intercalation of nucleoside monophosphates in a layered host material has been reported.[111] Nucleoside monophosphates can be intercalated into a variety of LDHs by simple ion-exchange processes. NMR experiments showed that a variety of LDHs ([Li-Al], [Mg-Al], [Zn-Cr] and [Ni-Al]) exhibit a strong preference for intercalating CMP from an equimolar solution of cytidine-5′-monophosphate (CMP) with either adenosine-5′-monophosphate (AMP) or guanosine-5′-monophosphate (GMP). Again temperature was found to have a role in determining the preference. For [Li-Al-Cl] LDH this selective intercalation property allows the recovery of the intercalated guest by washing the solid intercalate and the addition of dilute HCl to regenerate the host material and in this case the nucleotide thereby providing a cost effective, recyclable and tuneable simple separation technique (Fig. 6).

A remarkable example of a stereoselective intercalation reaction is provided by the ion-exchange of L- and D-histidine for $Cl^-$ in $[Mg_{0.7}Al_{0.3}(OH)_2](CO_3)_{0.15}\cdot nH_2O$ investigated by Ikeda *et al.*[41] The LDH was added to a solution of L- and D-histidine and the amounts of each intercalate determined indirectly from the concentration change in the supernatant solution upon addition of ninhydrin followed by colourimetry. Calculation of the rate of intercalation of the two isomers showed that the rate constant for L-histidine was larger. Hence stereoselective intercalation of the L-histidine was achieved by an optically inactive LDH, this property is most likely to be due to characteristics of the interlayer region.

## Mechanistic studies of intercalation reactions

A large variety of techniques can be used to characterise the products of intercalation reactions; elemental analysis, XRD, IR and NMR among others are all common techniques. *In situ* techniques are particularly useful as they allow the determination of the kinetics and mechanisms of the reactions. For example *in situ* techniques have been used to monitor the course of a variety of decomposition and intercalation reactions of LDHs. Pérez-Ramirez *et al.* used *in situ* infrared and *in situ* Raman spectroscopy to investigate the differences between the two decomposition processes for [Co-Al] and [Ni-Al] LDHs.[124,125]

*In-situ* X-ray diffraction is a very useful technique as it allows the simultaneous observation of the characteristic Bragg reflections and intensities of the peaks corresponding to reactants, intermediates (if any are formed) and products throughout a reaction. Examples of reactions that have been investigated using the Energy Dispersive X-Ray Diffraction (EDXRD) method include the formation of metal aluminium phosphates,[126–128] hydrothermal crystallisations of gallium oxyfluorophosphates,[129] the intercalation of metallocenes

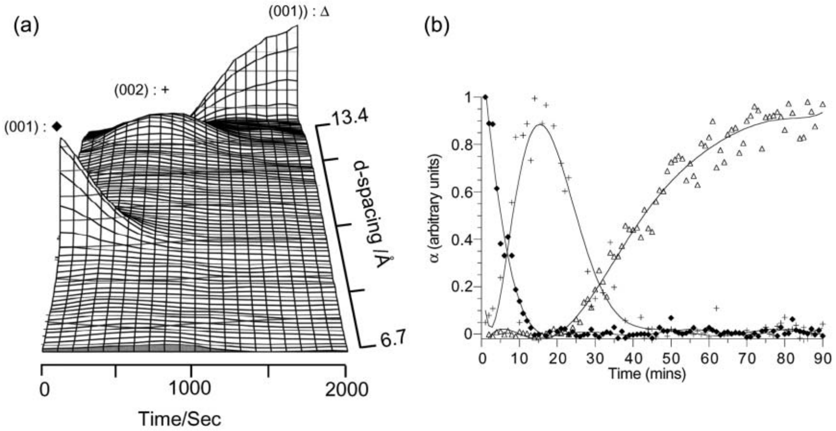


**Fig. 7** Time-resolved, *in situ*, energy dispersive X-ray powder diffraction data showing the course of the ion exchange reaction between $[LiAl_2(OH)_6]Cl\cdot H_2O$ and disodium succinate: (a) 3D stacked plot; (b) plot of integrated intensity of 001 reflection of the host (◆), 002 reflection of the 2nd stage intermediate (+) and 001 reflection of the final phase (Δ) as a function of time.

into layered metal dichalcogenide hosts and the anion exchange reactions of $[LiAl_2(OH)_6]Cl \cdot H_2O$.[30,130] *In situ* EDXRD studies on the intercalation of dicarboxylate anions into $[LiAl_2(OH)_6]Cl \cdot H_2O$ revealed that the reaction proceeded by the rapid formation of a second stage intermediate which then transforms into a phase pure fully ion-exchanged product (Fig. 7).[31]

The staging phenomenon is very rare for layered materials that are rigid such as in hydrotalcite-type minerals. These second stage intermediates can be isolated by reaction with a stoichiometric amount of the required guest. Similarly the competition intercalation reaction between terephthalate and phthalate into $[Ca_2Al(OH)_6]NO_3 \cdot 2H_2O$ has also been investigated.[17] The *in situ* XRD data reveal that 2 Bragg reflections due to both intercalation compounds form initially, however, the peak due to the phthalate quickly decreases in intensity as the peak due to the terephthalate intercalate grows and at the end of the reaction it is the sole product. The phthalate intercalate is a kinetic product which undergoes exchange with terephthalate in solution to form the thermodynamically favoured terephthalate intercalate.

## Conclusions

The very exciting recent developments in intercalation reactions of LDHs show that this area of contemporary solid state chemistry has a very promising future. In particular, the ongoing work on the intercalation of biologically active guests has great potential. In future years I foresee that LDHs will move from being used as simple low cost ion-exchange materials to being used as part of a sophisticated drug or gene delivery system in patient care or therapy.

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