Synthesis, characterization and applications of layered double hydroxides containing organic guests

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The use of layered inorganic solids as host materials for the creation of inorganic–organic host-guest supramolecular structures is of increasing interest. In this review we outline the preparation, characterization and uses of layered double hydroxides (LDHs) containing organic guests. LDHs consist of stacks of positively charged mixed metal hydroxide layers that require the presence of interlayer anions to maintain overall charge neutrality. A range of organic guests may be incorporated, including aliphatic and aromatic carboxylates, sulfonates and phosphonates as well as porphyrin and phthalocyanine derivatives. Potential applications of organo-LDHs in the areas of catalysis, sorption, photochemistry and electrochemistry are outlined. Overall, it is demonstrated that with LDHs it is possible to create, in a systematic manner, novel inorganic–organic supramolecular structures.

1 Introduction

Layered materials that are able to intercalate neutral guest molecules or to exchange inorganic and organic ions for interlayer ions have attracted considerable attention.[1–3] Through the incorporation of a guest species into a layered host, novel solids may be engineered with desirable physical and chemical properties. Various layered materials such as clay minerals, graphite, transition metal dichalcogenides, and metal phosphates and phosphonates have the ability to act as host materials. These materials have been studied as potential catalysts, selective sorbents and hosts for nanoscale reactions.[4–8] A particularly attractive feature of such layered hosts is that they serve as a template for the creation of intercalated supramolecular arrays. Layered double hydroxides (LDHs), also known as anionic clays, are host-guest materials that, owing to their potential application in these and other areas, have recently gained much attention.[9–11]

LDHs are available as naturally occurring minerals and as synthetic materials. They were first prepared in the laboratory in 1942 when Feitknecht[12,13] reacted dilute aqueous metal salt solutions with base, although the first detailed structural analyses of LDHs were not carried out until the late 1960s by Allmann[14,15] and Taylor[16,17] and their co-workers. Briefly, LDHs consist of stacks of positively charged mixed metal hydroxide layers that require the presence of interlayer anions to maintain overall charge neutrality. One subset of LDHs is that in which the charge balancing anion is organic. The incorporation of organic molecules into inorganic layered hosts in general has been extensively investigated[18,19] and presents a method of obtaining novel nanocomposite materials. This review discusses the preparation, properties and applications of organo-LDHs. In particular, we indicate the range of organic guests that may be incorporated into LDHs and describe how it is possible to create, in a systematic way, inorganic–organic supramolecular structures.

1.1 Structural properties of LDHs

The most important group of LDHs may be represented by the formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]A^{n-}{}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively; x is equal to the ratio $M^{3+}/(M^{2+}+M^{3+})$ and A is an anion of valence n. The structure of LDHs is most clearly described by considering the structure of brucite, $Mg(OH)_2$, which consists of Mg^{2+} ions co-ordinated octahedrally by hydroxyl groups. The octahedral units share edges to form infinite, charge neutral layers. In an LDH, isomorphous replacement of a fraction of the Mg^{2+} ions with a trivalent cation, such as Al^{3+}, occurs and generates a positive charge on the layers that necessitates the presence of interlayer, charge balancing, anions. The remaining free space of the interlayer is occupied by water of crystallization (Fig. 1).

Different stacking arrangements of the hydroxide layers are observed, giving rise to polytypism. The mineral of composition $Mg_6Fe_2(OH)_{16}(CO_3)\cdot 4H_2O$, for example, may have either a three-layer repeat (Pyroaurite, the 3R polytype) or a two-layer repeat (Sjögrenite, the 2H polytype).[17] An investigation of the polytype diversity of LDHs has recently been conducted.[20,21]

In general, M^{2+} and M^{3+} ions that have an ionic radius not too different from that of Mg^{2+} (ionic radius of $Mg^{2+} = 0.65$ Å) can be accommodated in the holes of the close-packed OH groups in the brucite-like layers to form LDHs. Observed M^{2+} and M^{3+} species include Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} or Zn^{2+} and Al^{3+}, Cr^{3+}, Ga^{3+} or Fe^{3+}, respectively. Furthermore, LDHs containing more than two species of the second cation have been prepared.[22,23] The charge density on the hydroxide layers of the LDH will clearly depend upon the M^{2+}/M^{3+} ratio. A particular advantage of LDHs, therefore, is that the anion-exchange capacity of the LDH, and hence the number and arrangement of the charge

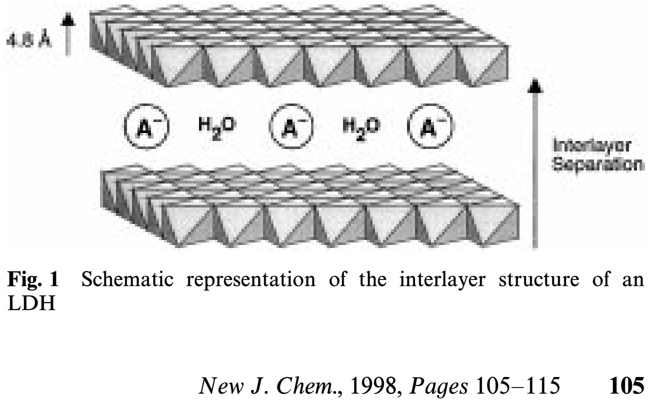

Fig. 1 Schematic representation of the interlayer structure of an LDH

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balancing anions in the LDH, may be controlled by varying the M^{2+}/M^{3+} ratio.

A second class of LDHs, which have not been as extensively studied, contains monovalent and trivalent matrix cations. An example is $[LiAl_2(OH)_6]^+A^- \cdot mH_2O$, which consists of sheets of aluminium octahedra with vacancies filled by lithium atoms.[24–27]

In naturally occurring LDHs, the most common anion found is carbonate. In practice, however, there is no significant restriction to the nature of the charge balancing anion that can occupy the interlayer region; for example, halides,[24,25,28,29] oxo-anions,[24,25,28,29] silicates,[30-32] polyoxometalate anions,[24,25,33–40] complex anions[41–43] as well as organic anions, may all be incorporated.

In the remainder of this review the composition of LDHs with divalent and trivalent cations will be represented with the convenient notation $M^{2+}M^{3+}(A)$, where A is the interlayer anion. Similarly, LDHs containing Li and Al matrix cations will be represented as LiAl(A).

1.2 Characterization of LDHs

A variety of techniques are used to characterize LDHs. Powder X-ray diffraction (PXRD) and infrared spectroscopy (IR), for example, are routinely used whilst others such as ESR,[44] XAS,[39,45,46] and computer modelling,[47,48] although reported, are less extensively employed.

The most frequently employed technique is PXRD. Diffractograms are normally obtained using randomly oriented powdered samples although in certain cases oriented samples or samples under solution have been studied (it will be seen in Section 3 that the diffractogram obtained for an organo-LDH is critically dependent upon the degree of hydration of the sample). A typical diffractogram obtained for an LDH consists of sharp basal (00*l*) reflections at low values of 2θ corresponding to successive orders of the interlayer spacing. In addition, relatively weak non-basal reflections at higher values of 2θ are present. In certain cases, the non-basal reflections are quite broad, which may be attributed to turbostratic disordering of the hydroxide layers.

Generally, the patterns are indexed on the basis of a hexagonal unit cell. The interlayer spacing of the LDH is equivalent to $1/n$ of the c parameter, where n is the layer repeat of the unit cell, which depends upon the stacking sequence of the layers. Subtracting the hydroxide layer thickness of approximately 4.8 Å from the interlayer spacing yields the gallery height (Fig. 1). The gallery height will depend on the size and orientation of the charge balancing anion.

The M^{2+}/M^{3+} ratio of the LDH may be inferred from the a parameter of the unit cell, which is determined using the relationship $a = 2d_{110}$, where d_{110} is the d spacing of the 110 reflection. For a MgAl LDH, for example, and as a result of the smaller ionic radius of Al^{3+} (0.50 Å) compared to Mg^{2+} (0.65 Å), the a parameter decreases as the aluminium content of the LDH increases. The measurement of d_{110} for determining the M^{2+}/M^{3+} ratio of the LDH, along with elemental analysis techniques, enables an approximate chemical formula for the LDH to be deduced. The possibility of precipitating $M(OH)_2$ and/or $M(OH)_3$ phases during synthesis, however, may mean that bulk chemical analysis would not be appropriate. Such phases may be amorphous and therefore not detected by PXRD.

IR is a useful technique for confirming the presence of the charge balancing anion in an LDH. The incorporation of a carboxylic acid anion into an LDH, for example, would be identified by strong antisymmetric and symmetric carboxylate stretching bands at approximately 1560 and 1400 cm^{-1}, respectively. Alternatively, intercalation of the undissociated acid form would be identified by the strong absorption of the carbonyl stretch of the acid at approximately 1700 cm^{-1}. In addition, IR allows the presence of impurity inorganic charge balancing anions, such as carbonate and/or nitrate, to be confirmed.

The thermal properties of organo-LDHs are commonly studied using thermogravimetry (TG), differential scanning calorimetry (DSC) and differential thermal analysis (DTA). In certain cases these techniques are used in combination with a mass spectral analyser, to study the nature of the evolved gases during the thermal treatment. The thermal properties of organo LDHs are discussed in Section 3.6.

2 Synthesis procedures

There are four general approaches to the preparation of organo-LDHs: (I) anion-exchange of a precursor LDH; (II) direct synthesis by coprecipitation; (III) rehydration of a calcined LDH precursor and (IV) thermal reaction. A common problem with all the methods is that in preparations of LDHs with anions other than carbonate it is important to avoid contamination from CO_2, since the carbonate anion is readily incorporated and tenaciously held in the interlayer. Consequently, decarbonated and deionized water is often used and exposure of the reacting material to the atmosphere is kept to a minimum.

The synthesis of LDHs containing carboxylic acid derivatives has recently been reviewed by Carlino.[49]

2.1 Anion exchange

The anion-exchange method is the most common method for the preparation of organo-LDHs. The anion-exchange properties of LDHs containing simple inorganic anions are well documented.[28,29,50] The ease of exchange of monovalent anions is in the order $OH^- > F^- > Cl^- > Br^- > NO_3^-$. Divalent anions such as SO_4^{2-} and CO_3^{2-} have higher selectivity than monovalent anions. LDHs containing nitrate anions are, therefore, the most suitable precursors for anion-exchange syntheses due to the relative ease with which the nitrate anions can be displaced from the interlayer. In general, the anion-exchange reaction is carried out by simply dispersing the precursor LDH in aqueous solution containing an excess of the organic anion that is to be incorporated. The organic anion of interest must be stable at the pH of exchange and, if the M^{2+}/M^{3+} ratio of the precursor LDH is to be retained in the anion-exchanged LDH, the hydroxide layers must also be stable.

Exchange of interlayer anions by an organic anion (acetate) was first reported by Miyata and Kumura[41] in 1973, although the publication gives no details of the characterization of the exchanged LDH. Later, Boehm *et al.*[51] reported the anion exchange of a ZnCr LDH containing nitrate or chloride anions with short- and long-chain sodium alkyl sulfate anions. A variety of organo-LDHs, with different combinations of matrix cations, as well as different interlayer organic anions, have been prepared by Meyn *et al.*[52] using an anion-exchange route.

A large variety of other organic molecules have been incorporated into LDHs using anion exchange. These include porphyrins functionalized with sulfonate or carbonate groups,[53–55] M^{II} phthalocyanines (M = Cu or Ni) functionalized with sulfonate groups,[42,56] malonate,[57] aromatic diphosphonate[37] and 5-benzoyl-4-hydroxy-2-methoxybenzensulfonate anions.[58] In addition, the incorporation of an anionic β-cyclodextrin derivative into a MgAl LDH *via* anion exchange has recently been reported.[59]

2.2 Direct synthesis by coprecipitation

The coprecipitation method for the direct synthesis of LDHs containing simple inorganic anions has been developed over a number of years[12,13,60–63] and a similar procedure is used for organo-LDHs: the M^{2+} and M^{3+} hydroxide layers are nucleated and grown from an aqueous solution containing the anion that is to be incorporated into the LDH. The anion that is to be introduced must have a high affinity for the hydroxide layers, otherwise the counter anions of the metal salts may be incorporated, thus contaminating the LDH. For this reason, metal nitrate or chloride salts are commonly utilized because of the low selectivity of LDHs towards these anions.[28]

In general, the coprecipitation is performed by adding an aqueous solution of the metal nitrate or chloride salts to an aqueous solution of the organic anion. Usually, the coprecipitation is performed at constant pH by simultaneously adding $NaOH_{(aq)}$. A particular advantage of the coprecipitation method is that it allows for accurate control of the charge density (M^{2+}/M^{3+} ratio) on the hydroxide layers of the product LDH. In order to ensure simultaneous precipitation of the matrix cations it is necessary to perform the synthesis at a pH at which both the M^{2+} and M^{3+} hydroxides precipitate. To ensure that the M^{2+}/M^{3+} ratio in the starting solution is retained in the product LDH it is important to control the pH. Without pH control, the formation of impurity $M(OH)_2$ and/or $M(OH)_3$ phases, and consequently a product LDH with an undesired M^{2+}/M^{3+} ratio, is probable.[64,65] It has been reported that the optimum coprecipitation pH is dependent upon the combination of matrix cations utilized and the organic anion present.[11,66] To obtain phase-pure LDHs generally only M^{2+}/M^{3+} ratios between 2 and 4 are possible (*i.e.*, values of x in the range 0.33–0.2).[10] Ratios lower than 2 lead to a high density of M^{3+} octahedra in the hydroxide layer, which act as nuclei for the formation of $M(OH)_3$; similarly, at ratios higher than 4 the formation of $M(OH)_2$ is probable. The usual direct synthesis procedure involves crystallization of the coprecipitation product for 18 h at a temperature in the region of 65–75 °C. In certain cases, however, this does not lead to a well-crystallized organo-LDH phase, in which case hydrothermal treatment may be used to improve the crystallinity of these materials.[67,68]

2.3 Rehydration of calcined LDH precursor

Miyata[69] reported that a hydrotalcite-like LDH [$MgAl(CO_3)$] transforms into a mixed magnesium aluminium oxide after heat treatment at 500–800 °C, which rehydrates and combines with anions to re-form a LDH in the presence of water and anion. This so-called *memory effect* property of LDHs provides an effective synthetic route for inserting inorganic and organic anions into LDHs. An advantage of this method is that the incorporation of competing inorganic counter anions into the LDH is prevented, although the inclusion of carbonate from atmospheric CO_2 remains a problem. The ease and extent of reconstruction of the calcined LDH are controlled by the properties of the matrix cations as well as the temperature of calcination.[70,71]

The reconstruction of an LDH from a mixed metal oxide precursor is believed to occur *via* a topotactic reaction. To improve the crystallinity of the rehydrated product, therefore, Carlino *et al.*[72] recommend heating the precursor LDH using a slow ramping technique (~ 1 °C min^{-1}). This technique prevents the rapid expulsion of carbon dioxide and water from the LDH, which occurs upon direct and sudden heating, disrupting the layered structure of the calcined product.

Chibwe and Jones[43] used the rehydration method to prepare a series of MgAl LDHs containing various organic anions. In certain cases impurity $MgAl(CO_3)$ phases were detected in addition to the corresponding organo-LDH phase. If the rehydration is performed in a nitrogen atmosphere carbonation of the product LDH may still remain a problem due to the high affinity of the mixed oxide for carbonate anions.[73]

Dimotakis and Pinnavaia[74] showed that the use of glycerol as a swelling agent assists the incorporation of the organic guests *via* the rehydration route. In this procedure, a 1 : 2 (v/v) water–glycerol solution was used for the reconstruction of a calcined $MgAl(CO_3)$ precursor in a nitrogen atmosphere. The reaction products obtained were single phase and crystallographically well-ordered. In the absence of glycerol mixed phases were observed.

A variety of organo-LDHs have been prepared *via* the rehydration route, including LDHs containing naphthalenecarboxylate[75] or cobalt^{II} phthalocyaninetetrasulfonate anions.[44,76,77]

2.4 Thermal reaction

Thermal reaction is a relatively new approach to the preparation of organo-LDHs. The procedure was first reported in 1994 by Carlino and Hudson[78] who reacted molten sebacic acid with a $MgAl(CO_3)$ LDH. In this procedure an intimate mixture of $MgAl(CO_3)$ and sebacic acid was heated at a temperature 20–30 °C above the melting point of the acid.

A similar procedure for incorporating the caprate or phenylphosphonate anions into a MgAl LDH was also used.[72,79] In addition to the corresponding organo-LDH phase, the thermal reaction product was found to contain in each case an unreacted $MgAl(CO_3)$ phase. Although phase-pure organo-LDH products have not been obtained using thermal reaction, this approach nevertheless provides an interesting alternative to the conventional *wet* methods.

3 Organization of anions within the LDH

3.1 Aromatic carboxylate anions

Organo-LDHs in which the charge balancing anion is an aromatic carboxylate anion are among the most widely studied systems. LDHs containing terephthalate[33,34,39,40,47,52,64–68,73,80–86] or benzoate[42,52,64–68,73,83,84,87] anions in particular have received much attention. For terephthalate anions an interlayer spacing of between 14.0 and 14.4 Å, corresponding to a gallery height of between 9.2 and 9.6 Å, is generally reported for a variety of matrix cations and synthesis methods. The physical length of the terephthalate anion, including the van der Waals radii of the terminal oxygen atoms, is approximately 9.9 Å. Allowing for the fact that the terminal oxygen atoms of the terephthalate anion are most likely hydrogen bonded to the hydroxide layers, dimensional analysis suggests that for such a spacing the terephthalate anion adopts an orientation with its long axis perpendicular to the hydroxide layers.

For LDHs containing the benzoate anion, a gallery height of between 10.4 and 10.7 Å is generally observed. The length of the benzoate anion, including van der Waals radii of the terminal oxygen and hydrogen atoms is approximately 8.8 Å and two interlayer arrangements of the benzoate anion have been proposed to account for the observed gallery height. First is a bilayer-like structure with the carboxylate groups of the anions attached to adjacent inwardly facing hydroxide layers and the aromatic groups interleaved within the mid-plane of the gallery.[64,65,68] Moggridge *et al.*[87] have suggested, from NEXAFS measurements, that in this arrangement the benzoate anion is inclined at an angle of $35 \pm 10°$ to the hydroxide surface of the layers. Alternatively, a vertical arrangement in which a water molecule is retained between the benzene ring and the hydroxide surface has been suggested.[52]

Kooli *et al.*[64,65] have investigated the properties of a series of MgAl LDHs containing terephthalate or benzoate anions and possessing varying layer charge (*i.e.*, varying Mg/Al ratio). Two extreme orientations were observed for the organic anions between the hydroxide layers: either vertical (*i.e.*, gallery heights of approximately 9.2 and 10.4 Å for terephthalate or benzoate, respectively) or horizontal. For the terephthalate or benzoate anions in a horizontal orientation a gallery height of approximately 3.5 Å was observed, approximately the thickness of a benzene ring.

At room temperature, it was found that the orientation of the terephthalate anion is dependent upon the charge density on the layers and the degree of hydration of the LDH. For samples prepared with initial Mg/Al ratios of 1 or 2, PXRD indicated that the terephthalate anion adopts a vertical orientation (interlayer spacing = 14.2 Å) before and after drying. For the sample prepared with an initial Mg/Al ratio of 3, the same vertical orientation was observed before drying. After drying in air overnight at 60 °C, however, it was found that the terephthalate anion adopts a horizontal orientation, as determined by a reduction of the interlayer spacing from 14.2 to 8.3 Å. This process was found to be completely reversible upon repeated cycles of drying and rehydration.

The apparent change in orientation of the terephthalate anion with increasing Mg/Al ratio demonstrates that a balance of forces determines the adopted interlayer arrangement of the anion. Coulombic repulsion and anion packing density, which are dependent upon the M^{2+}/M^{3+} ratio, are important factors. For a rigid, linear dicarboxylate anion such as terephthalate a vertical monolayer arrangement allows for maximum separation of the positively charged layers, whilst also maintaining a strong interaction between the anion and the layers. This arrangement also ensures maximum lateral separation between the anions in the interlayer. The charge density on the hydroxide layers of the LDH decreases with increasing Mg/Al ratio and hence there is a lower packing density of the anions at high Mg/Al ratios (*e.g.*, Mg/Al ratio 3), which allows the terephthalate anions to adopt a horizontal orientation in the interlayer. In addition, coulombic repulsion between the hydroxide layers will be reduced as the Mg/Al ratio of the LDH increases. The ability of excess water to maintain the vertical orientation of the terephthalate anion at Mg/Al ratio 3 indicates that hydrophobic/hydrophilic interactions are also important.

The existence of a $\sqrt{3}a$ hexagonal superlattice in the *ab* plane for a MgAl LDH containing benzoate anions and prepared with an initial Mg/Al ratio of 2 has recently been reported.[67,68] The formation of a superlattice could result from an ordered distribution (*i.e.*, no Al^{3+} neighbouring each other) of the cations within the hydroxide layer, and has also been reported for a MgAl LDH containing sulfate anions.[21] Furthermore, the observation of a superlattice suggests an ordered distribution of the interlayer anions, since Al and Mg have similar scattering powers. Cation ordering in synthetic LDHs, including a MgFe LDH containing benzoate has recently been investigated by Vucelic *et al.*[88]

3.2 Aliphatic carboxylate anions

A series of ZnAl LDHs containing terminal linear aliphatic dicarboxylates, $C_nH_{2n}(CO_2^-)_2$, was prepared by direct synthesis by Miyata and Kumura.[41] The interlayer spacing of the organo-LDH was found to increase linearly from 9.4 Å for oxalate ($n = 0$) to approximately 18–19 Å for sebacate ($n = 8$) (Fig. 2). The gallery height of the ZnAl(sebacate) LDH, obtained by subtracting the brucite layer thickness of 4.8 Å from the interlayer separation, is close to the physical length of the sebacate anion. Dimensional analysis suggests, therefore, that the sebacate anion is oriented with its long axis approximately perpendicular to the hydroxide layers in a monolayer arrangement.

Chibwe and Jones[43] reported interlayer spacings of 16.3 and 18.8 Å for a MgAl LDH containing the sebacate anion prepared *via* rehydration and coprecipitation routes, respectively. Similarly, Carlino and Hudson[78] observed interlayer spacings of 19.3 and 17.6 Å for the same material prepared *via* thermal reaction and coprecipitation, respectively. These interlayer spacings are also consistent with a monolayer arrangement of the sebacate anion between the hydroxide layers. The range of values observed, however, show that the interlayer spacing of the organo-LDH depends on the history (*e.g.*, the method of synthesis and drying conditions *etc.*) of the product. The differences between the values observed may be due to additional inclusion of water or to small differences in the orientation and packing of the alkyl chains (possibly as a result of different layer charge densities on the product LDHs). Carlino and Hudson[78] attributed the different separations that they observed to a change in the angle of orientation (from 90° to approximately 60°) of the sebacate dianion with respect to the surface of the hydroxide layers.

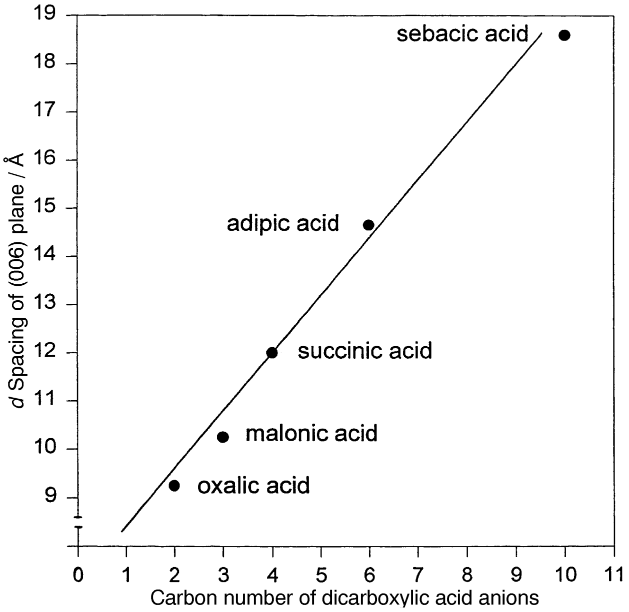

Fig. 2 Relationship between carbon number of dicarboxylic acid anions and the *d* spacing of the (006) plane of the organo-LDH (after Miyata and Kumura[41])

A linear relationship between the observed interlayer spacing and the chain length of linear aliphatic dicarboxylates was also reported by Meyn *et al.*[52] for series of ZnCr and ZnAl LDHs. The interlayer spacing of $ZnCr(NO_3)$ increased from 8.9 to 9.9 Å when oxalate anions were exchanged for the interlayer nitrate anions. The interlayer spacing was then found to increase linearly with the chain length of the exchanged anion up to 18.0 Å for sebacate. A similar linear relationship was observed by Raki *et al.*[89] for a MgFe LDH containing a series of linear dicarboxylate anions (from $n = 0$ to 12), prepared *via* coprecipitation.

An analogous trend is reported by Meyn *et al.*[52] for a ZnCr LDH containing a series of linear aliphatic monocarboxylates, $C_nH_{2n+1}CO_2^-$, prepared *via* an anion-exchange route. The interlayer spacing was found to increase linearly from 11.2 Å for formate ($n = 0$) to 31.6 Å for nonadecanoate ($n = 18$). It is important to note, however, that the interlayer spacings were determined for the LDH in equlibrium with the exchange solution. Upon drying in air (30–60 °C), it was found that the layer structure becomes poorly ordered and the intensity of the basal reflections is significantly reduced. The disordering was attributed to decarboxylation of the anions.

For a linear monocarboxylate anion the formation of a vertical bilayer arrangement is probable because the interlayer of a LDH has two ionic surfaces, top and bottom, to which the carboxylate group is equally likely to attach. The bilayer may be arranged with the alkyl chains of the anions end-to-end or interleaved. In addition, the anion may also be inclined at an angle from the normal to the layers. Carlino and Hudson[79] prepared a MgAl LDH containing the caprate anion ($n = 9$) *via* a coprecipitation route. The interlayer separation, after air-drying at room temperature, was found to be 19.6 Å, which was attributed to the formation of an end-to-end bilayer-like arrangement with the caprate anion at a slant angle of 38° to the surface of the hydroxide layers.

3.3 Sulfates and sulfonates

A large number of different organic anions containing sulfate (SO_4^-) or sulfonate (SO_3^-) groups have been incorporated into LDHs. A series of alkyl sulfate anions, $C_nH_{2n+1}SO_4^-$, for example, was incorporated into a ZnCr LDH *via* anion exchange by Boehm *et al.*[51] The products of the exchange were found to have basal spacings in the range 21.1 ($n = 8$) to 32.6 Å ($n = 18$) and underwent substantial additional swelling in the presence of *n*-alkyl alcohols or *n*-alkylamines. A detailed study of alkyl sulfate anions incorporated *via* anion exchange into ZnCr LDHs has been carried out by Kopka *et al.*[90] It was proposed that the alkyl sulfate anions adopt monolayer arrangements between the hydroxide layers. In equilibrium with the exchange solution, a near perpendicular orientation of the alkyl chains was proposed. Following washing and drying at 60 °C, however, a reduction in the interlayer spacing revealed that the chains adopt a slant angle of 56° to the surface of the hydroxide layers.

The incorporation of dodecyl sulfate anions, $CH_3(CH_2)_{11}SO_4^-$, into series of NiAl, MgAl and ZnCr LDHs with varying layer charge has been studied by Clearfield *et al.*[91] For comparison, the dodecyl sulfate anion was incorporated *via* two methods: anion-exchange and coprecipitation. Depending upon the method of preparation, the products yielded interlayer spacings distributed about three mean values: 26, 36 and 47 Å. The different spacings revealed the existence of three different interlayer arrangements of the dodecylsulfate anion, with the shortest interlayer spacing (26 Å) corresponding to a perpendicular monolayer arrangement of the anion. Similar values have been obtained by other researchers for LDHs containing the dodecylsulfate anion.[33,51] The interlayer spacing of approximately 36 Å was attributed to a bilayer arrangement in which the anion is tilted at an angle of approximately 40° to the surface of the hydroxide layers. An alternative suggestion, that an interleaving vertical bilayer arrangement is adopted by the dodecylsulfate anion, was also proposed. The 47 Å spacing was considered consistent with a vertical end-to-end bilayer arrangement.

A particularly interesting result has been reported for an LDH containing secondary alkanesulfonates.[52] The anions are a mixture of different isomers, with the sulfonate group positioned at different carbon atoms along the alkyl chain. The PXRD pattern obtained for this organo-LDH shows several orders of sharp basal reflections, indicating that the layer structure is extremely well-ordered, *i.e.*, the interlayer spacing is highly regular. This is a surprising result considering that the charge balancing anions have different structures. The result was explained, however, by assuming that the alkanesulfonates adopt a U-shaped conformation and are in a bilayer arrangement. Thus, the differently shaped alkanesulfonate ions may pair up in such a way that a constant layer separation is obtained (see Fig. 3).

A series of ZnAl LDHs, each containing a different isomer of the naphthalenedisulfonate anion, have been prepared.[81] The relationship between the physical size of the incorporated anion and the interlayer spacing was investigated by changing the positions of the two sulfonate groups on the naphthalene moiety. A small difference in interlayer spacing was observed for the three isomers studied, which suggests a small dependence of the interlayer arrangement of the naphthalenedisulfonate anion on the positions of the two sulfonate groups.

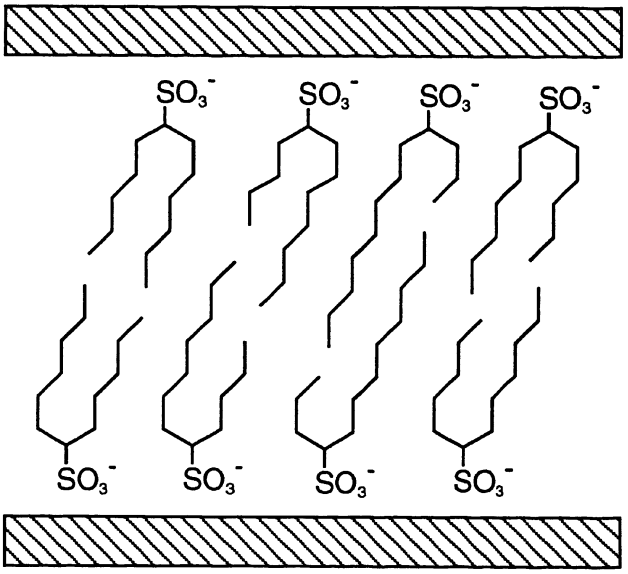

Fig. 3 Formation of bilayers consisting of isomers of secondary alkanesulfonates between the hydroxide layers of an LDH (after Meyn *et al.*[52])

The incorporation of 9,10-anthraquinone-2,6-disulfonate anions into a MgAl LDH led to two distinct conformations of the organic anion.[92] The LDHs were prepared *via* coprecipitation (using a controlled pH of 10–11) with various initial Mg/Al/organic anion ratios. The products were single phase with, depending on the orientation of the anion, interlayer spacings of approximately 19 or 12 Å. The 19 Å phase was selectively obtained under Al-rich preparation conditions, although the initial Mg/Al ratio was not retained in the product LDH. It was found that the Mg/Al ratio of the product LDH, as determined by chelatometric titration, depends neither on the phase to which the sample belongs nor the initial ratio in the sample preparation. (It should be noted, however, that an *a* parameter of 3.02 Å was reported for the 19 Å phase, whereas an *a* parameter of 3.06 Å was reported for the 12 Å phase. This would seem to suggest that the 19 Å phase is, in fact, Al-rich compared with the 12 Å phase. The resulting different layer charge densities of the two phases would then account for the different interlayer arrangements observed.)

Franklin *et al.*[58] reported the presence of three distinct and interconvertible phases when the 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonate (BHMBS) anion was incorporated into a ZnAl LDH. The selected anion is dibasic, having both a strong sulfonate group and a much weaker phenolate group. It was found that anion exchange of the divalent anion (in which both the sulfonic and phenolic groups are ionized) formed an LDH with an interlayer spacing of 13.8 Å. The monovalent form (in which only the sulfonic group is ionized) yielded an LDH with an interlayer spacing of 20 Å and readily converted to the divalent form within the LDH. The observed different interlayer spacings revealed that the guest molecule occupies two distinct conformations within the interlayer, depending upon the charge of the anion. Furthermore, it was found that the divalent phase may be converted into a 15.4 Å phase, which is intermediate between the monovalent and divalent forms, by exposure of the LDH to water vapour, or by dispersion in low pH (pH ≈ 6) solution (Fig. 4).

Cai *et al.*[93] used atomic force microscopy to investigate the adsorption of the BHMBS anion onto the surface of a MgAl LDH. It was found that the packing arrangement and orientation of the BHMBS anion, adsorbed on the surface of the LDH layers in aqueous solution, are governed by factors such as coulombic and hydrogen bonding interactions between the anion and the positively charged LDH surface.

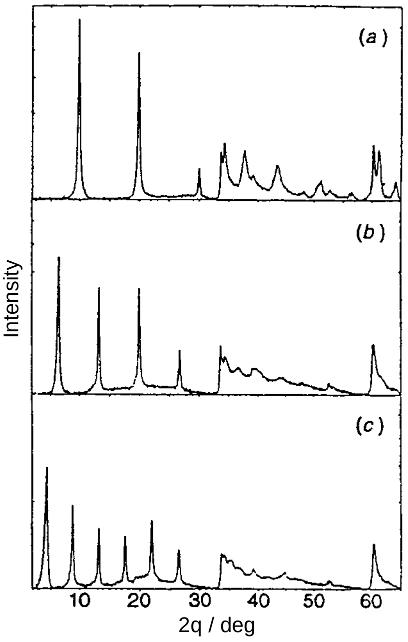

Fig. 4 PXRD pattern of ZnAl LDHs: (*a*) ZnAl(NO$_3$), (*b*) 13.8 Å phase ZnAl(BHMBS), (*c*) 20 Å phase ZnAl(BHMBS) (Franklin *et al.*,[58] reproduced by permission of the Royal Society of Chemistry)

The incorporation of quite large organic molecules containing sulfonate groups into LDHs has been reported. An example is 5,10,15,20-tetra(4-sulfonatophenyl)-porphyrin (TSPP), which has been anion-exchanged into a MgAl LDH.[54] The interlayer spacing of 22.4 Å (along with IR and visible spectra) suggest that the molecule is inserted intact with the molecular planes perpendicular to the hydroxide layers (Fig. 5).

3.4 Phosphonates

The preparation of organo-LDHs containing aromatic phosphonates has recently been reported. Anion exchange of the benzenediphosphonate anion, $[O_3P{-}C_6H_4{-}PO_3]^{4-}$, into a MgAl LDH was found to depend upon the temperature at which the reaction was performed.[37] If the exchange was performed at ≈0 °C, PXRD revealed a single, crystallographically well-ordered product LDH phase, with an interlayer spacing (14.7 Å) corresponding to a perpendicular monolayer arrangement of the diphosphonate anion. If the exchange was carried out at room temperature, a second phase with a smaller interlayer spacing (9.6 Å) was observed, in addition to the 14.7 Å phase. This additional phase was attributed to dehydration of the OH groups of the hydroxide layer and subsequent attachment of the phosphonate groups directly to the metal cations in the layers, *i.e.*, no longer through the layer surface OH groups. For the products of the exchange reaction carried out above room temperature, or if any of the products were dried rigorously, the phase with the smaller interlayer spacing was found to predominate. Carlino *et al.*[72] have also reported the existence of a MgAl LDH containing the phenylphosphonate anion, in which it is proposed that the phosphonate group is connected directly to the matrix cations.

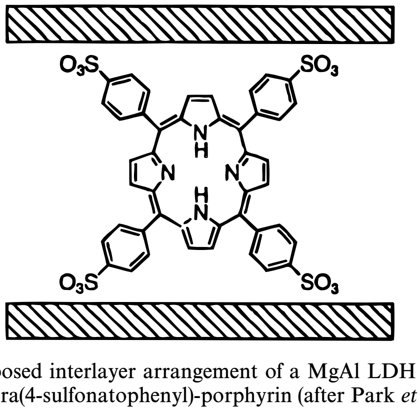

Fig. 5 Proposed interlayer arrangement of a MgAl LDH containing 5,10,15,20-tetra(4-sulfonatophenyl)-porphyrin (after Park *et al.*[54])

In addition, Vichi and Alves[94] have recently investigated the anion-exchange reactions of CdAl(NO$_3$) and CdAl(CO$_3$) with phenylphosphonic acid and 2-carboxyethylphosphonic acid.

3.5 Polymeric anions

The preparation of LDHs containing organopolymers has received growing attention in recent years. Tanaka *et al.*[95] prepared a MgAl LDH containing polyacrylate anions, *via* the *in situ* polymerization of interlayer acrylate anions. The acrylate anions were incorporated *via* anion exchange and the subsequent polymerization was carried out by the addition of an initiator (potassium peroxodisulfate) to the undried product followed by heat treatment for 1 day at 80 °C. The polymerization of the acrylate anion was inferred by the disappearance of the absorption band due to C=C double bond stretching in the infrared spectrum of the organo-LDH, following the heat treatment. In addition, the interlayer spacing decreased from 13.8 to 13.4 Å upon polymerization of the acrylate anion. The PXRD pattern of the MgAl LDH containing polyacrylate revealed a poorly crystalline material. Sugahara *et al.*[96] have reported the preparation of a MgAl LDH containing polyacrylonitrile using a similar procedure. An *in situ* polymerization route has also been used for the preparation of a CuCr LDH containing polyaniline.[80] In this case, the oxidative polymerization of aniline intercalated in a CuCr(terephthalate) LDH is reported.

Oriakhi *et al.*[97] describe the preparation and characterization of a series of LDHs containing a variety of matrix cations and three vinylic polymers: polyacrylate, polyvinylsulfonate and polystyrenesulfonate. The organopolymer LDHs were coprecipitated in a basic solution containing the dissolved polymer. Interlayer spacings of between 12.0 and 21.6 Å were determined for the reaction products, indicating incorporation of the polymer, although the broad basal reflections observed indicate poor crystallinity of the products. A bilayer arrangement of the anionic polymers was proposed. A similar method was used by Messersmith and Stupp[98,99] for intercalating water soluble organopolymers into a CaAl LDH. In these methods, a preformed polymer is incorporated between the hydroxide layers of the LDH.

Whilton *et al.*[100] have recently prepared a MgAl(polyaspartate) LDH *via* two synthetic routes: *in situ* thermal polycondensation of MgAl(aspartate) and direct synthesis in the presence of the preformed polymer. In both cases, however, the crystallinity of the LDH product is poor.

3.6 Thermal characteristics

The thermal stability of LDHs is an important consideration for many potential applications. Consequently, the thermal characteristics of LDHs containing various charge balancing anions have received considerable attention.[29,64,67,69,91,99,101–109]

In general, the thermal decomposition of organo-LDHs can be divided into three stages: (I) the removal of physisorbed water at the surface and between the hydroxide layers, from room temperature to approximately 300 °C; (II) dehydroxylation of the hydroxide layers in the range 300–500 °C and (III) elimination and combustion of the organic anion. The precise temperature at which each stage starts and finishes depends on many factors, including the nature of M^{2+} and M^{3+}, the M^{2+}/M^{3+} ratio and the nature of the anion. In particular the

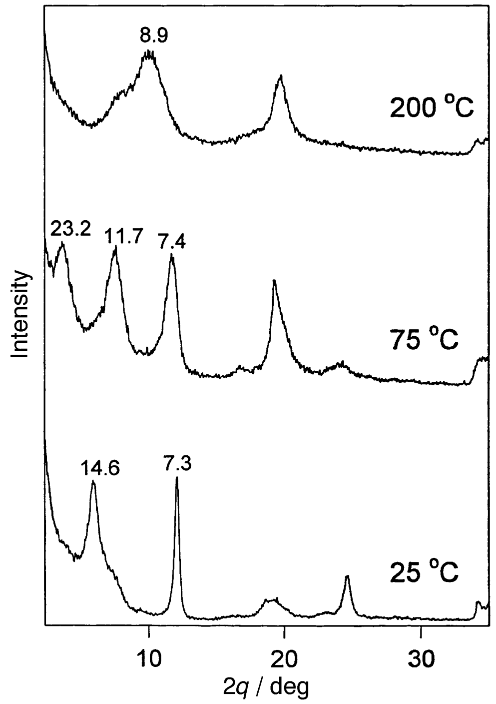

Fig. 6 Temperature dependence of the PXRD patterns obtained for MgAl(terephthalate) prepared with a Mg/Al ratio of 2, after heat treatment at different temperatures. The reflection at 23.2 Å is associated with the creation of an interstratified arrangement of vertical and horizontal terephthalate anions (after Kooli *et al.*[64])

temperature at which stage III occurs can vary considerably and depends upon the identity of the organic anion. For a MgAl(terephthalate) LDH, for example, elimination of the organic anion occurs above 500 °C.[64] For a MgAl(dodecyl sulfate) LDH, however, elimination of the organic anion occurs at much lower temperature, in the range 150–300 °C.[91] The difference between the two systems may be attributed to the strength of the interaction between the organic anion and the hydroxide layers. Kuwahara *et al.*[106] have investigated the thermal properties of a MgAl LDH containing *p*-toluenesulfonate anions. It was found that the organic anion contained within the LDH was easier to decompose than the anion in the form of its sodium salt. It was considered that this effect is due to the existence of a stronger interaction between sodium and *p*-toluenesulfonate than between the LDH and the anion.

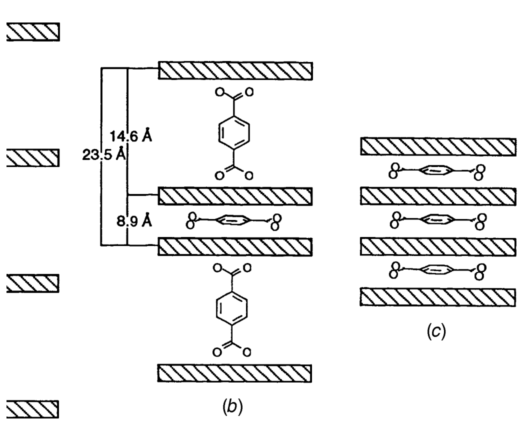

Fig. 7 Proposed model for structural changes occurring during the heat treatment and loss of interlayer water of the LDH described in Fig. 6 at (*a*) 25, (*b*) 100 and (*c*) 200 °C (after Kooli *et al.*[64])

The thermal properties of a CaAl LDH intercalated with polyvinylalcohol have been studied by Messersmith and Stupp.[99] The intercalate has an interlayer spacing of approximately 18 Å at room temperature, which persists upon heating to at least 400 °C. The organopolymer intercalate heated to 1000 °C transforms into an inorganic solid that has a different phase composition than the unintercalated LDH heated to the same temperature.

The effect of thermal treatment on the interlayer arrangement of a MgAl(terephthalate) LDH has recently been investigated by Kooli *et al.*[64] using PXRD at elevated temperatures. The LDH was prepared *via* coprecipitation from an initial Mg/Al ratio of 2. At room temperature it was found that the terephthalate anion is in a vertical orientation between the hydroxide layers. Above 150 °C (a temperature at which water loss becomes important) the expanded structure collapses, as was determined by a shift in the position of the 003 reflection from 14.6 to 8.9 Å, suggesting a horizontal arrangement for the anion. At intermediate temperatures, *e.g.*, at 75 °C, reflections at 23.2, 11.7 and 7.4 Å were observed (Fig. 6). The reflection at 23.2 Å was rationalized in terms of an ordered interstratification of collapsed and expanded layers, with the *d* spacing of the lowest angle reflection close to the sum of the *d* spacings of the 003 peak of the vertical form at room temperature and the *d* spacing of the horizontal form at 150 °C (Fig. 7).[64,67]

A low temperature (<150 °C) thermal analysis of a LiAl(myrisate) LDH has been performed by Borja and Dutta.[107] Incorporation of the myrisate anion was achieved *via* exchange in ethanol. At room temperature, a monolayer arrangement of the myrisate anions is formed with an interlayer spacing of 22 Å. The interlayer spacing expands to 43 Å at 100 °C, with removal of the solvent (ethanol), and the anion adopts a vertical bilayer arrangement. The non-expanded state was re-formed by cooling and redispersing the LDH in ethanol. A molecular explanation of this phenomenon is given by Dutta and Robins.[108] Borja and Dutta[107] also examined the low temperature thermal properties of a MgAl LDH intercalated with myristic acid. It was found that the interlayer spacing decreases from 39 to 24 Å upon heating from room temperature to 140 °C, through the formation of irregularities in the all-*trans* bilayer conformation of the alkyl chains. The as-prepared form could not be re-formed by cooling or treatment with ethanol, unlike the LiAl system. The high temperature (up to 450 °C) thermal properties of the LiAl(myrisate) LDH have been studied by Jakupca and Dutta.[109]

4 Applications of organo-LDHs

The applications of LDHs (and their thermal decomposition products) containing inorganic charge balancing anions are well documented.[10] There is a wide range of applications for these materials, although the major application is in the field of catalysis. It will be seen in this Section that there is also a variety of potential applications for organo LDHs.

4.1 Catalytic applications

Reichle[110] has investigated the catalytic behaviour of the thermal decomposition products of a number of LDHs containing a variety of matrix cations and charge balancing anions. In general, the products are fairly strong bases and useful catalysts for vapour-phase aldol condensations. It was found that the thermal decomposition products of LDH precursors containing organic anions such as 1,10-decanedicarboxylate, 1,12-dodecanedicarboxylate or oxalate anions showed improved activities for the aldol condensation of acetone compared with the thermal decomposition products of carbonate-LDH precursors.

The incorporation of inorganic polyoxometalate anions, such as $[V_{10}O_{28}]^{6-}$ and $[Mo_7O_{24}]^{6-}$, into LDHs has received considerable attention.[33,34,36,38,74,104,111–113] Such polyoxometalate LDHs may represent a class of pillared materials for selective adsorption and oxidation catalysis. Although the direct synthesis of an LDH containing polyoxometalate anions has recently been reported,[36,111] earlier work by Drezdzon[33] demonstrated that the incorporation of these inorganic anions could be achieved *via* an intermediate MgAl(terephthalate) LDH. Acidifying the organo-LDH in the presence of $NaVO_3$, for example, leads to the simultaneous polymerization of the monovanadate and displacement of the terephthalate from the interlayer, resulting in the incorporation of the polyoxovanadate ($[V_{10}O_{28}]^{6-}$) species. The use of a terephthalate LDH intermediate avoids the problems that may be associated with exchanging a small anion such as nitrate with a large polyoxometalate anion.

Evans *et al.*[39] recently investigated the incorporation of polyoxometalate anions into LDHs *via* directly synthesized LDH precursors containing terephthalate, *p*-methylbenzoate or *p*-hydroxybenzoate. The most suitable organic anion for exchange with the polyoxometalate was found to be *p*-methylbenzoate.

There has been increasing interest[44,56,76,77,114] in supporting metallophthalocyanines on LDHs, owing to the fact that these macrocyclic complexes can function as biomimetic catalysts for the autoxidation of organic molecules in aqueous solution. Cobalt(II) phthalocyaninetetrasulfonate ($[CoPcTs]^{4-}$), for example, is active for the autoxidation of a thiolate to a disulfide.[77] Incorporation of the phthalocyanine complex into a MgAl LDH was found to significantly improve the catalyst reactivity (Fig. 8) and longevity for this reaction, compared to the homogeneous catalyst.[77] In addition, the use of an LDH support affords easy removal of the catalyst from the reaction medium. The same material is also active for the autoxidation of 2,6-di-*tert*-butylphenol to the corresponding diphenoquinone,[76] and the reductive dehalogenation of certain halogenated organic compounds.[114] In addition, Shannon *et al.*[46] have recently studied the oxidation of cyclohexene over a ZnAl LDH containing $[CoPcTs]^{4-}$. Metallophthalocyanine complexes supported on LDHs, therefore, have a potential application in the treatment of waste water *via* the degradation of organic pollutants. Similar materials based on the incorporation of metalloporhyrins into LDHs have also been investigated.[44,53,54,115]

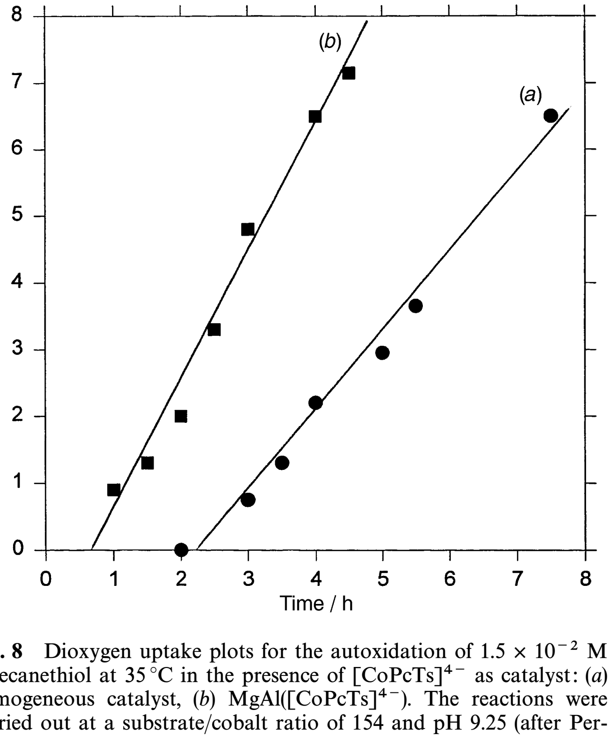

Fig. 8 Dioxygen uptake plots for the autoxidation of 1.5×10^{-2} M 1-decanethiol at 35 °C in the presence of $[CoPcTs]^{4-}$ as catalyst: (*a*) homogeneous catalyst, (*b*) MgAl($[CoPcTs]^{4-}$). The reactions were carried out at a substrate/cobalt ratio of 154 and pH 9.25 (after Perezbernal *et al.*[77])

The use of organo-LDHs as precursors to LDHs with enhanced thermal stability has recently been reported.[116] The layer structure of a MgAl(CO_3) LDH prepared *via* reconstruction of a calcined organo-LDH precursor in $Na_2CO_{3(aq)}$ was found to collapse at a temperature approximately 100 °C above that of the layer structure of a MgAl(CO_3) LDH prepared *via* direct synthesis. The improved thermal stability of the layer structure was attributed to the presence of carbonaceous residues in the calcined organo-LDHs.

4.2 Photochemistry

The photophysical and photochemical properties of intercalation compounds, including smectites, zirconium phosphates and LDHs have recently been reviewed by Ogawa and Kuroda.[7] The interlayer region of LDHs provides a novel environment for photochemical reactions of photoactive molecules. The photochemistry of cinnamate anions between the hydroxide layers of a MgAl LDH, for example, has also been studied.[117] It was found that both photodimerization and photoisomerization of the cinnamate anions occurs between the layers.

The controlled photodimerization of a variety of unsaturated carboxylates between the hydroxide layers of a MgAl LDH has been reported by Takagi *et al.*[118] *Syn* head-to-head cyclodimers were selectively formed in the irradiation of sodium cinnamates between the hydroxide layers, whereas two isomers of *syn* head-to-head and *syn* head-to-tail cyclodimers were formed for the case of phenylethenylbenzoates. The product selectivity was shown to be controlled by the packing of the anions in the interlayer. Furthermore, the same authors have recently communicated that the photodimerization products can to some extent be controlled by changing the Mg/Al ratio, and hence the packing density of the incorporated monomer, of the host LDH.[119]

The incorporation of photochromic molecules into LDHs may yield useful photoresponsive materials. Tagaya and coworkers[120,121] have studied the photoisomerization of sulfonated indolinespirobenzopyran ($SP\text{-}SO_3^-$) to merocyanine (MC) in the interlayer region of a MgAl LDH. The photoisomerization was found to be irreversible for a MgAl LDH containing $SP\text{-}SO_3^-$ due to the stability of MC in the polar environment of the hydroxide layers. In the presence of *p*-toluenesulfonate (PTS), however, the reversible photoisomerization between $SP\text{-}SO_3^-$ and MC in the interlayer region of the MgAl LDH was observed. Fig. 9 shows the proposed mechanism for the reversible photoisomerization between $SP\text{-}SO_3^-$ and MC in the MgAl(PTS) LDH.

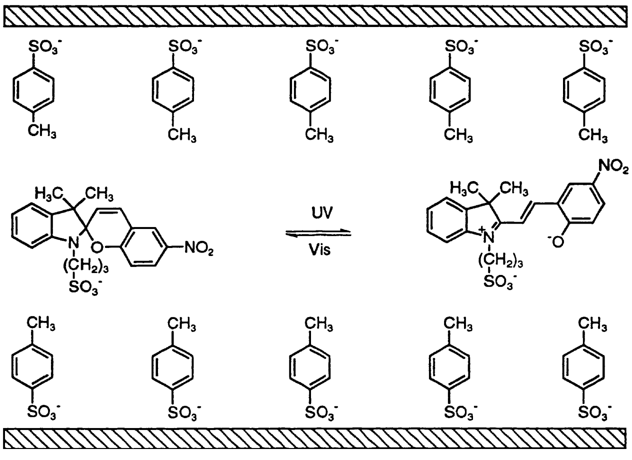

Fig. 9 Possible mechanism for the reversible photoisomerization between $SP\text{-}SO_3^-$ and MC in the interlayer of a MgAl(PTS) LDH (after Tagaya *et al.*[121])

The incorporation of anionic dyes into LDHs may yield materials with potential applications as pigments.[122] However, only a few preparations of LDHs containing anionic dyes have been reported.[28,122]

Second harmonic generation is a frequency-doubling nonlinear optical process. Cooper and Dutta[123] have prepared a LiAl LDH intercalated with 4-nitrohippuric acid, which exhibits second harmonic generation: 532 nm radiation from incident 1064 nm radiation. The ability of the intercalated material to exhibit nonlinear optical properties is due to a perpendicular monolayer packing of the acid molecules in the interlayer. This orientation leads to an ordered arrangement of dipoles, giving rise to a bulk dipole moment in the solid. Crystals of the pure acid exhibit no frequency-doubling characteristics due to a centrosymmetric packing in the crystal.

An examination of a LiAl LDH containing myrisate anions as a support for photochemical assemblies has recently been performed by Robins and Dutta.[55] The goal of the study was to assemble a LDH containing TiO_x in which the TiO_x particles are able to interact with an anion-exchanged porphyrin. The incorporation of TiO_x in the interlayer was achieved by taking advantage of the hydrophobic nature of the organo-LDH, *i.e.*, titanium butoxide was partitioned into the interlayer, followed by hydrolysis under ambient conditions. A suggested application for such a system is in the photodegradation of pollutants.

4.3 Adsorption

The hydrophobic nature and accessibility of the interlayer region of organo-LDHs makes these materials candidates for the adsorption of other organic molecules. A ZnCr LDH containing alkyl sulfate anions, for example, undergoes swelling perpendicular to the layers under *n*-alkyl alcohols or *n*-alkylamines.[51] In addition, Kopka *et al.*[90] have found that ZnCr LDHs containing surfactant anions have the ability to take up a large variety of small organic molecules into the interlayer such as ethylene glycol, propanediol and glycerol.

Novel membrane-like materials are formed upon the incorporation of organic anions into LDHs.[107] These materials are of relevance to separation and membrane technologies. A LiAl LDH containing myrisate or hexanoate anions, for example, has the ability to partition pyrene from a methanol–water solution containing the polycyclic aromatic (Fig. 10).[124] No sorption of pyrene was observed for a LiAl(succinate) LDH, however, and this was attributed to a sieving effect of this compound towards the pyrene molecule. The sorption of polyaromatic hydrocarbons, such as pyrene, is important from an environmental perspective. It should be noted that calcined LDHs may also be used as absorbents of organic molecules in environmental applications.[125] In addition, the potential application of a LiAl(myrisate) LDH as a stationary phase in gas chromatography has been investigated, owing to the partitioning effect exhibited by this material.[109]

The adsorption properties of organo-LDHs may be utilized for the preparation of new materials. The intercalation of C_{60} molecules into the hydrophobic interlayer of a MgAl(dodecyl sulfate) LDH has recently been reported.[126] It was found that heating the resulting compound under vacuum to decompose the dodecyl sulfate left C_{60} molecules sandwiched between the hydroxide layers, although the crystallinity of the sample was poor.

A MgAl(terephthalate) LDH has been used for a novel method of studying the initial stages of the emulsifier-free emulsion polymerization of styrene.[82] The method involved trapping the negatively charge polystyrene oligomers from the polymerization reaction mixture. It was found that the terephthalate anions were rapidly exchanged for the charged oligomers.

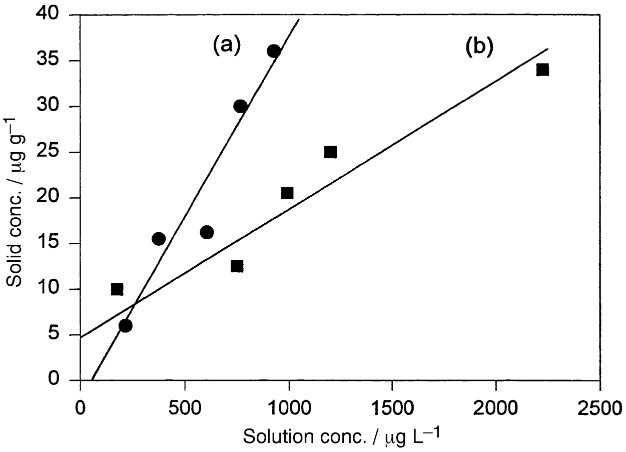

Fig. 10 Isotherm data for the uptake of pyrene in 50% methanol–water for (*a*) LiAl(myrisate) LDH, (*b*) LiAl(hexanoate) LDH (after Dutta and Robins.[124])

4.4 Electrochemistry

The potential application of organo-LDHs as new modified electrodes has been investigated.[127–134] Electroactive materials derived from LDHs containing organic electroactive molecules, such as anthraquinonesulfonates and *m*-nitrobenzenesulfonate, have been prepared by Mousty *et al.*[133] The electroactive anion was exchanged into a ZnCr LDH and a thin film of the product deposited on a glassy carbon electrode. The electrochemical behaviour of the substrate was then studied using cyclic voltammetry. It was found that these materials have potential applications for new clay-modified electrodes. The potential of ZnCr and ZnAl LDHs containing the electroactive 2,2′-azinobis-3-ethylbenzothiazoline-6-sulfonate anion as clay-modified electrodes has also been established by Therias and Mousty.[134] The electrochemical behaviour of manganese porphyrins incorporated into a MgAl LDH has also briefly been studied.[132]

4.5 Miscellaneous

The surface modification of LDHs with organic molecules has recently been reported.[135] It was found that the product of the reaction of a ZnAl(OH) LDH with an organic oxychloride is an esterified LDH, with the organic molecules attached directly to the cationic layer (*i.e.*, not through the surface OH

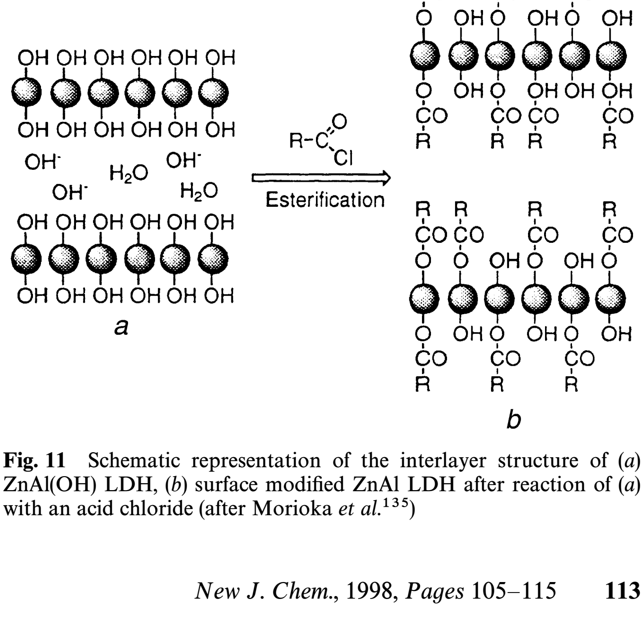

Fig. 11 Schematic representation of the interlayer structure of (*a*) ZnAl(OH) LDH, (*b*) surface modified ZnAl LDH after reaction of (*a*) with an acid chloride (after Morioka *et al.*[135])

groups) (Fig. 11). It has been suggested that these materials are candidates for new functional materials and catalysts.[135] Similarly, the preparation of modified MgAl LDHs, in which organophosphonate anions are connected directly to the cationic layer, has recently been reported.[37,72]

Finally, it is worth noting that organo-LDHs have been linked to prebiotic chemistry and may, therefore, have had a role to play in the origin of life.[68,136,137]

5 Concluding remarks

In this review we have concentrated on the host-guest supramolecular arrangements that form using layered double hydroxides. The observed chemistry complements that reported for cationic clay systems. In addition to organic guests it is also possible to incorporate, as alluded to in the text, complex polyoxoanions. Particularly important is the way that the disposition of the anions within the interlayer can be modified by changing the charge on the layers, the degree of hydration and the method of synthesis. The studies described here point to the possibility of creating novel inorganic–organic supramolecular arrangements with desired structural and chemical properties.

Acknowledgements

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