

Chapter 1

Introduction

1.0 Intercalation Chemistry

Intercalation in a chemical sense can be defined as the insertion of a guest between layers in a crystal lattice or other structure. The process is a topochemical one, in which minimal atomic and molecular displacement should occur and it should be reversible through appropriate chemical or thermal means.¹

There are many reports of intercalation in the scientific literature, with its origins suggested to date from as early as 600-700 AD when first used by the Chinese in the production of porcelain.² The first systematic studies focussed on the intercalation compounds of graphite³ and later transition metal dichalcogenides^{4, 5} and these have been the subject of a number of reviews.⁶⁻⁹ Since this time intercalation chemistry has continued to be an area of great scientific interest as a route by which the physical properties of a material can be tuned. As such, intercalation reactions and compounds have found applications in a range of diverse fields, including superconductors,¹⁰⁻¹² catalysis,^{13, 14} high-energy rechargeable lithium batteries¹⁵ and as volatile organic compound (VOC) sensors.¹⁶ Indeed the rational design of new materials able to fluoresce upon intercalation of nucleic acids is currently an area of increased interest as it is envisaged that such materials would be valuable in biochemical sensing technologies for forensics, medical diagnosis and bioterrorism prevention.¹⁷

A pertinent example of intercalation is known to occur between base pairs in DNA (Figure 1).¹⁸ The most efficient ligands are those with extended electron-deficient aromatic moieties which facilitate the extending and unwinding of the deoxyribose-phosphate backbone whilst they themselves are stabilised by π - π stacking interactions with the purine and pyrimidine-based chains.¹⁹ These changes can be fully reversed once the intercalated molecule is removed providing the DNA structure is not damaged by conditions required for removal, for example in DNA-acridine complex.²⁰

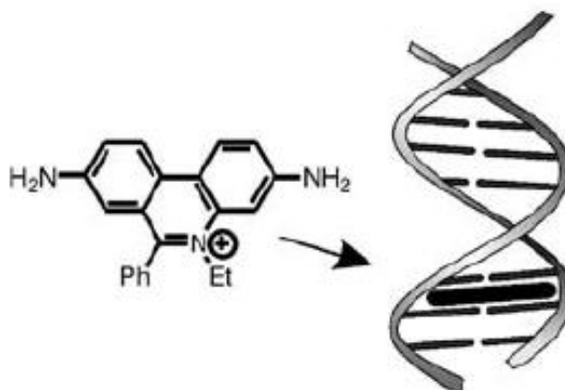


Figure 1 Intercalation of the well known DNA-binding dye ethidium bromide between two base pairs.¹⁸

Metallo-intercalators are metal complexes that possess suitable aromatic moieties. They can be used as investigative probes to monitor interactions with DNA and more general nucleic acid chemistry owing to their rich photochemical properties. The aromatic ligands are able to stack within the DNA sequence and act as a new base pair. $[\text{Ru}(\text{phen})_2(\text{dppz})]^{2+}$ exhibits solvatochromic luminescence in organic solutions and luminesces upon addition to DNA, as intercalation occurs the surrounding duplex prevents the access of water and hence characteristic emission is observed (Figure 2). Interestingly, whilst Ru-based complexes are found to act efficiently as so-called ‘molecular light switches’, Rh-based complexes are found to facilitate strand-scission upon photoexcitation.²¹

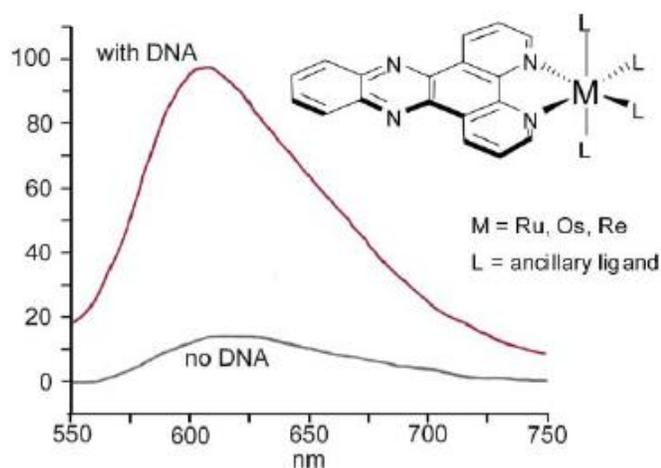


Figure 2 The light switch effect demonstrated by dppz-based metallo-intercalators.²¹

A wide range of materials are known to undergo intercalation reactions and these will be discussed further in the following section.

1.1 Intercalation Materials

Intercalation materials are described by their dimensionality rather than their chemical composition and these are shown in Figure 3.

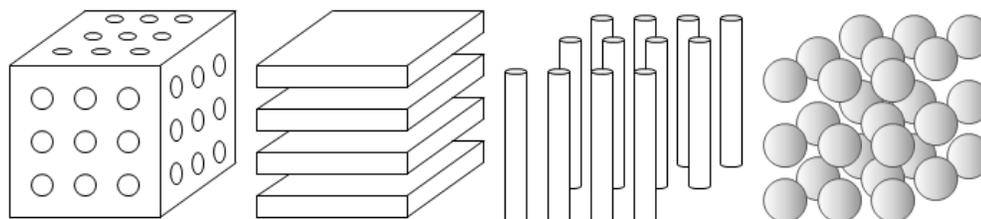


Figure 3 The basic host lattice dimensionalities; 3-D, 2-D, 1-D and 0-D (adapted from *Inorganic Materials*, Wiley, Chichester, 1996).²²

Cheetham *et al.* define hybrid inorganic-organic frameworks as those materials which contain inorganic and organic components as integral parts of a network with infinite bonding connectivity in at least one dimension.²³ In hybrid inorganic-organic materials dimensionality can be defined according to metal-ligand connectivity or extended inorganic connectivity, with most systems displaying both. Cheetham and co-workers have recently suggested a system by which this structurally diverse range of materials may be placed in context, Figure 4.

Some materials, including silicate and aluminosilicate minerals (simple silicate units, pyroxenes, clays, quartz) and metal phosphonates²⁴ demonstrate a range of dimensionalities from 0-3D.²³ 3-Dimensional frameworks typically have rigid structures and are characterised by the presence of channels and pores of fixed diameter, so that the guest size is restricted. These materials can be purely inorganic, e.g. zeolites²⁵ or hybrid systems as in metal-organic frameworks (MOFs)^{26, 27} and have applications in catalysis, separation and gas storage. 2-D materials consist of covalently bonded layers with weak non-covalent bonding in between the sheets, into which guest molecules can insert. As a result these materials offer increased flexibility in terms of guest size over their 3-D counterparts. Layered metal phosphates and phosphonates,²⁸⁻³⁰ layered double hydroxides^{31, 32} and clays^{33, 34} are the most widely studied lamellar intercalation materials and are used as sensors, catalysts and ion-exchangers.

Dimensionality of inorganic connectivity, I^n ($n = 0-3$)

	0	1	2	3
0	Molecular complexes I^0O^0	Hybrid inorg. chains I^1O^0	Hybrid inorg. layers I^2O^0	3-D Inorg. hybrids I^3O^0
1	Chain coordination polymers I^0O^1	Mixed inorg.–organic layers I^1O^1	Mixed inorg.–organic 3-D framework I^2O^1	—
2	Layered coordination polymers I^0O^2	Mixed inorg.–organic 3-D framework I^1O^2	—	—
3	3-D Coordination polymers I^0O^3	—	—	—

Figure 4 Cheetham's proposed classification of hybrid materials, showing the dimensionality of different structures with respect to organic connectivity between metal centres (O^n) and extended inorganic connectivity (I^n).²³

In 1-D systems linear chains are separated by van der Waals interactions with the gaps between the chains providing empty lattice sites. This results in increased flexibility over layered materials but lower structural stability, giving rise to lattice defects and increased disorder. Niobium triselenide, $NbSe_3$ comprises chains of face sharing trigonal prismatic $[NbSe_6]$ units and has been shown to form Li_3NbSe_3 with *n*-BuLi.^{35, 36} Ternary molybdenum dichalcogenides result from the condensation of Mo_6Se_6 clusters to form infinite chains, the intercalation of alkali metals stabilizes the structure and $Tl_2Mo_6Se_6$ is superconducting.³⁷ Finally, molecular lattices (0-D systems) consist of discrete units, the reaction of alkali metals with C_{60} to give superconducting materials can be considered as an intercalation reaction of this type (A_3C_{60} , $A = K, Rb, Cs$).³⁸ In addition, reactions with neutral molecules³⁹ as well as oxidative intercalation⁴⁰ have been demonstrated.

It is the flexible 2-dimensional materials which will form the basis of this thesis and the composition, structure, synthesis and applications of layered hydroxides will be reviewed herein.

1.2 Layered Hydroxide Anion Exchange Materials

Layered hydroxides are a class of materials which comprise positively-charged metal hydroxide layers with exchangeable charge-balancing anions residing in the interlayer gallery. The layered hydroxides may be sub-divided into the layered double hydroxides (LDHs), hydroxy double salts (HDSs), hydroxy nitrate salts and layered rare-earth hydroxides (LRHs). The LDHs however, dominate the field as the most studied family with greater than 90 % of literature reports in this area pertaining to their synthesis, characterisation and intercalation chemistry.

1.3 Structure

1.3.1 Layered Double Hydroxides (LDHs)

The first LDH to be discovered was the naturally occurring mineral hydroxalite in the 19th century. Its exact composition, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ however was not reported until 1915.⁴¹ Subsequent single crystal X-ray diffraction studies revealed two polytypes of this structure; hexagonal with the stacking sequence *aba* and rhombohedral with an *abca* stacking sequence as shown in Figure 5.⁴² Single crystal X-ray diffraction work by Allmann and Taylor showed that the structure comprised the two cations within the same layer with the anions and water molecules between.^{43, 44} The layered double hydroxides are important as they are materials that comprise positively charged layers, and hence are also termed “anionic clays” in the literature.⁴⁵ The charge-balancing anions between the layers are exchangeable.

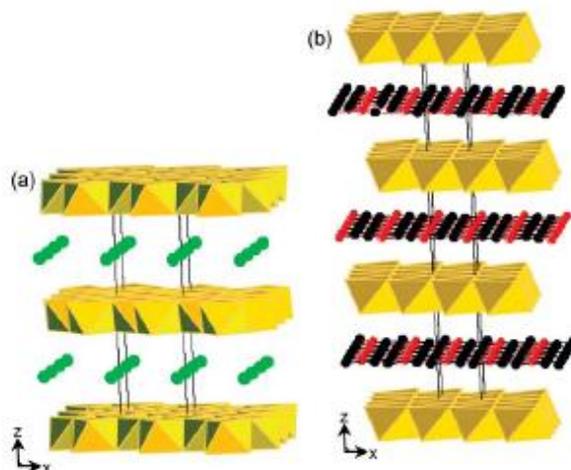


Figure 5 General structure of an LDH showing the two possible polymorphic stacking patterns: (a) hexagonal, (b) rhombohedral.⁴⁶

The LDHs are structurally related to brucite [$\text{Mg}(\text{OH})_2$], (Figure 6a) which is based on metal-hydroxide octahedra which edge-share to form two-dimensional sheets. Partial substitution of the divalent cations with trivalent cations generates a net positive charge of the layers. The layers stack together by hydrogen-bonding with hydroxy groups in neighbouring sheets with charge-balancing anions and water molecules residing in the interlayer space. The materials possess great compositional flexibility as both metals as well as the intercalated anion can be varied.

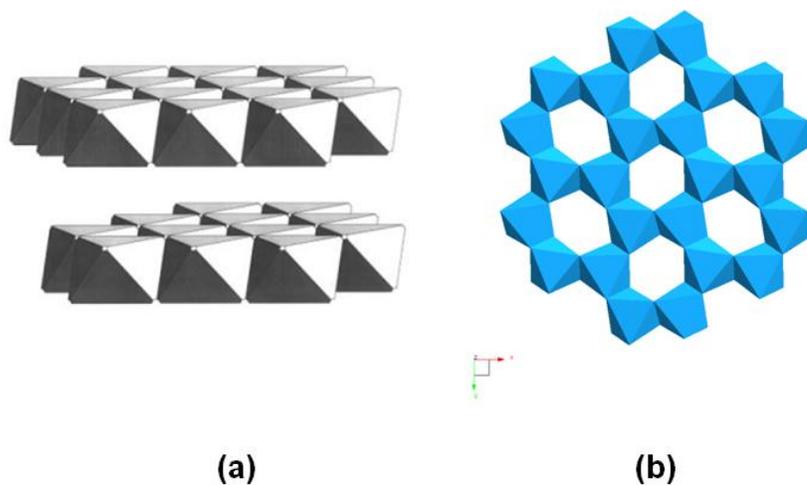


Figure 6 Structures of (a) brucite⁴⁷ and (b) gibbsite layer.⁴⁸

The structure and composition of LDHs has been the subject of detailed reviews.^{46, 49, 50} The materials can be described by general formula $[M^{z+}_{1-x}M^{3+}_x(OH)_2]^{\zeta+}(A^{n-}_{\zeta/n})_m \cdot mH_2O$, with $M^{3+} = Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Ga^{3+}, Co^{3+}$ or Ni^{3+} and where $z = 2$, $M^{2+} = Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}$ or Fe^{2+} . Where $z = 1$, $M^+ = Li^+$ and $M^{3+} = Al^{3+}$ giving $\zeta = 2x - 1$. Values of x are in the range $0.1 \leq x \leq 0.5$, with pure phases found only in the range $0.2 \leq x \leq 0.33$.⁵¹ Where x values exceed this range, different phases are formed.^{52, 53} For MgAl-LDHs it has been postulated that high values of x lead to the formation of $Al(OH)_3$ due to an increased number of aluminium octahedra. Conversely, low values of x result in the formation of $Mg(OH)_2$ resulting from increased magnesium octahedra.⁵⁴ In terms of ionic radii, M^{2+} cations are generally in the range $0.65 - 0.80 \text{ \AA}$, whilst M^{3+} are typically $0.62 \leq r(M^{3+}) \leq 0.69 \text{ \AA}$ (with the exception of Al^{3+} for which the radius is 0.50 \AA). The compositional flexibility of the layer structure is illustrated in Figure 7.⁵⁵ Given that octahedral coordination within the layers is required for the formation of these materials, smaller metal cations such as Be^{2+} and the larger metal cations ($Sc^{3+}, Cd^{2+}, Ca^{2+}, La^{3+}$ and Ba^{2+}) are generally unsuitable.⁵⁶⁻⁵⁸ Ti^{3+} -containing LDHs are known not to form, owing to the instability of this oxidation state. V^{3+} has been incorporated into LDHs by Kooli *et al.*⁵⁹ and Rives *et al.*^{60, 61} Y^{3+} has been incorporated in to LDH layers by Fernandez *et al.* ($MgAlY-NO_3$).⁶²

hydrogen 1 1.008																	helium 2 4.0026	
lithium 3 6.941	beryllium 4 9.0122											boron 5 10.811	carbon 6 12.011	nitrogen 7 14.007	oxygen 8 15.999	fluorine 9 18.998	neon 10 20.180	
sodium 11 22.990	magnesium 12 24.305											aluminum 13 26.982	silicon 14 28.086	phosphorus 15 30.974	sulfur 16 32.065	chlorine 17 35.453	argon 18 39.948	
potassium 19 39.098	calcium 20 40.078	scandium 21 44.956	titanium 22 47.88	vanadium 23 50.942	chromium 24 52.004	manganese 25 54.938	iron 26 55.845	cobalt 27 58.933	nickel 28 58.693	copper 29 63.546	zinc 30 65.38	gallium 31 69.723	germanium 32 72.64	arsenic 33 74.922	selenium 34 78.96	bromine 35 79.904	krypton 36 83.80	
rubidium 37 85.468	strontium 38 87.62	yttrium 39 88.906	zirconium 40 91.224	niobium 41 92.906	molybdenum 42 95.94	technetium 43 [98]	ruthenium 44 101.07	rhodium 45 102.905	palladium 46 106.42	silver 47 107.868	cadmium 48 112.411	indium 49 114.818	tin 50 118.710	antimony 51 121.757	tellurium 52 127.60	iodine 53 126.905	xenon 54 131.29	
cesium 55 132.91	barium 56 137.33	* 57-70	lutetium 71 174.967	hafnium 72 178.49	tantalum 73 180.96	wolfram 74 183.84	reuterium 75 186.21	osmium 76 190.23	iridium 77 192.22	platinum 78 195.084	gold 79 196.967	mercury 80 200.59	thallium 81 204.38	lead 82 207.2	bismuth 83 208.98	polonium 84 [209]	astatine 85 [210]	radon 86 [222]
francium 87 [223]	radium 88 [226]	** 89-102	lawrencium 103 [261]	rutherfordium 104 [261]	dubnium 105 [262]	seaborgium 106 [266]	bohrium 107 [264]	hassium 108 [268]	meitnerium 109 [269]	unnilennium 110 [271]	ununennium 111 [272]	unbinilium 112 [277]	ununseptium 114 [289]					
lanthanum 57 138.91	cerium 58 140.12	praseodymium 59 140.91	neodymium 60 144.24	promethium 61 [145]	samarium 62 150.36	europium 63 151.96	gadolinium 64 157.25	terbium 65 158.93	dysprosium 66 162.50	holmium 67 164.93	erbium 68 167.26	thulium 69 168.93	ytterbium 70 173.04					
actinium 89 [227]	thorium 90 232.04	protactinium 91 231.04	uranium 92 238.03	neptunium 93 [237]	plutonium 94 [244]	americium 95 [243]	curium 96 [247]	berkelium 97 [247]	californium 98 [251]	fermium 99 [257]	mendelevium 100 [258]	nobelium 101 [259]	lawrencium 102 [260]					

Figure 7 Metals incorporated into LDH layers, red outline indicates literature reports (adapted from *Quim. Nova*, 2004, 27, 601).⁵⁵

Gibbsite (see Figure 6b) is one of four naturally occurring polymorphs of $\text{Al}(\text{OH})_3$, a fifth high pressure phase is also known. LDHs derived from $\text{Al}(\text{OH})_3$ can be hexagonal (gibbsite) or rhombohedral (bayerite and norstrandite). In gibbsite-based layered double hydroxides Al^{3+} ions occupy octahedral holes in alternate layers of hexagonal close packed sheets of hydroxyl ions. In order to maintain a charge neutral sheet, one third of the octahedral sites lie vacant. A positively charged layer is achieved by the incorporation of additional cations into these vacant sites. In this way, these materials are particularly important as they demonstrate unique capability to exchange both cations and anions into the host lattice. An example of a hexagonal LDH derived from gibbsite is $[\text{LiAl}_2(\text{OH})_6]\text{A}$ ($\text{A} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-$), for which the crystal structure is shown in Figure 8.⁶³ Similarly the rhombohedral form $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ can be prepared.⁶⁴ A class of layered double hydroxides with the layer composition $[\text{MAl}_4(\text{OH})_{12}]\text{A}_n\cdot y\text{H}_2\text{O}$, ($\text{M} = \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}$ and Co^{2+}), have also been synthesised.⁶⁵

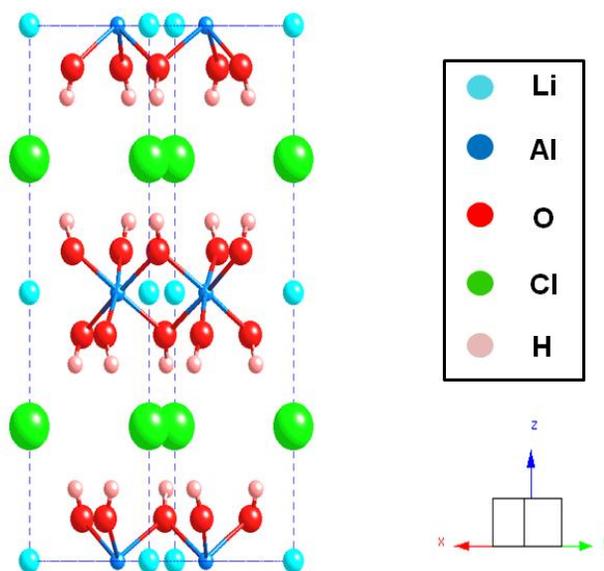


Figure 8 $[\text{LiAl}_2(\text{OH})_6]\text{Cl}$ (after dehydration to remove coordinated water).⁶³

Until recently knowledge of the ordering of metal cations within the hydroxide layers in many LDHs remained elusive, however a recent solid state NMR study has revealed Mg/Al ordering in LDHs.⁶⁶ The authors applied a combination of high-resolution ^1H -NMR and ^1H - ^{27}Al double-resonance and ^{25}Mg triple-quantum MAS NMR data to show that cations are ordered across a range of Mg/Al ratios.

1.3.2 Hydroxy Double Salts (HDSs)

The hydroxy double salts (HDSs) are another class of lamellar materials with the host lattice comprising two divalent cations in the hydroxide layer. They can be described by the general formulae $(M^{2+}N^{2+})_5(OH)_8(A^{n-})_{2/n}$ or $[(M^{2+}_{1-x}N^{2+}_{1+x})(OH)_{3(1-y)/n}]^+ A^{n-}_{(1+3y)/n} \cdot zH_2O$. The HDSs are less tolerant towards differences in ionic radii than the LDHs, as Table 1 shows, the difference in the radii of M^{2+} and N^{2+} does not exceed 0.05 Å.

Table 1 Ionic Radii of Metal Ions in LDHs and HDSs.⁶⁷

Layered Double Hydroxides			Hydroxy Double Salts		
Cations	Radii (Å)	Difference (Å)	Cations	Radii (Å)	Difference (Å)
Li ⁺ , Al ³⁺	0.68, 0.51	0.17	Zn ²⁺ , Co ²⁺	0.74, 0.72	0.02
Zn ²⁺ , Cr ³⁺	0.74, 0.63	0.11	Zn ²⁺ , Ni ²⁺	0.74, 0.69	0.05
Cu ²⁺ , Cr ³⁺	0.72, 0.63	0.09	Zn ²⁺ , Cu ²⁺	0.74, 0.72	0.02
Cu ²⁺ , Al ³⁺	0.72, 0.51	0.21	Ni ²⁺ , Cu ²⁺	0.69, 0.72	0.03
Zn ²⁺ , Al ³⁺	0.74, 0.51	0.23	Cu ²⁺ , Co ²⁺	0.72, 0.72	0.00
Mg ²⁺ , Al ³⁺	0.66, 0.51	0.15			
Ni ²⁺ , Al ³⁺	0.69, 0.51	0.18			
Ca ²⁺ , Al ³⁺	0.99, 0.51	0.48			

It is perhaps surprising that anion exchange occurs for HDSs, given that no net charge can result from the substitution of M^{2+} with N^{2+} in the brucite structure. In the case of those containing nitrate e.g. $[Cu_2(OH)_3NO_3]$, this behaviour results from the exchange of anions incorporated into the hydroxide layer. The structure comprises $[Cu_2(OH)_4]$ layers in which 25 % of the hydroxide anions have been replaced by nitrate. An oxygen atom from a nitrate group occupies the position of one hydroxide ion of the layer with the remaining two residing in the interlayer gallery and these oxygen atoms form single layers between the $[Cu_2(OH)_3]^+$ layers.⁶⁸

The other form of HDS which undergo anion exchange is $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (shown in Figure 9).⁶⁹ The anion exchange potential of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ has been demonstrated by reaction with aqueous metal chloride solutions.⁷⁰ $[\text{Zn}_5(\text{OH})_8]\text{Cl}_2 \cdot \text{H}_2\text{O}$ has also been described by several groups.^{42, 43, 68, 69, 71} Within the zinc hydroxide layers 25 % of the octahedral positions are empty with Zn^{2+} occupying the tetrahedral positions above and below the vacant sites. Zinc atoms are in an octahedral:tetrahedral ratio of 3:2. The octahedrally coordinated Zn^{2+} are surrounded by 6 hydroxy groups and the tetrahedral Zn^{2+} are coordinated to 3 hydroxy groups and a water molecule. As a result the layers have a net positive charge which is balanced by chloride anions residing in the interlayer space.

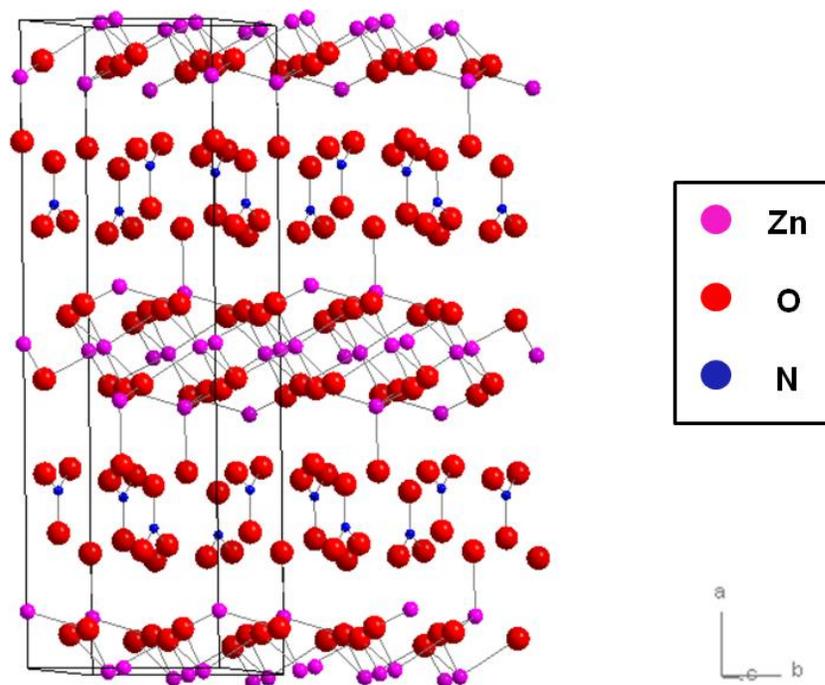


Figure 9 Structure of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

The hydroxy double salts can be further divided into three groups; zinc copper hydroxy acetate (ZCA) $\text{Cu}_{3.6}\text{Zn}_{1.4}(\text{OH})_{7.6}(\text{CH}_3\text{CO}_2)_{2.4} \cdot 5\text{H}_2\text{O}$, zinc nickel hydroxy acetate (ZNA) $\text{Zn}_{3.2}\text{Ni}_{1.5}(\text{OH})_{7.9}(\text{CH}_3\text{CO}_2)_{1.5} \cdot 1.7\text{H}_2\text{O}$ and zinc hydroxy acetate (ZHA) $\text{Zn}_5(\text{OH})_8(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$.⁷² Hossenlopp and co-workers investigated the kinetics of the room temperature anion exchange reactions of these materials through energy-

dispersive X-ray diffraction.⁷³ The rate constants for acetate release were strongly influenced by the size of the in-coming anion and the structure and composition of the host material. For the intercalation of butyrate into ZCA a rate constant of $k = 2.6 \times 10^{-3} \text{ s}^{-1}$ and for octanoate $k = 0.8 \times 10^{-3} \text{ s}^{-1}$ were reported. However the butyrate anion intercalates fully (98 %) whereas only 58 % conversion is observed for octanoate. Reactions between ZHA and octanoate proceed at a faster rate but do not reach completion.

1.3.3 Hydroxy Nitrate Salts and Layered Rare Earth Hydroxides (LRHs)

The larger lanthanides are known to form layered hydroxynitrates with the general formula $\text{Ln}(\text{OH})_2\text{NO}_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd}$ and Y ; $x = 0, 1$)⁷⁴⁻⁷⁷ Structural investigations by both Haschke and Mullica *et al.* demonstrate that the materials form a monoclinic dihydroxide mononitrate at or below 400 °C.^{77, 78} Haschke reports lattice parameters for $\text{Y}(\text{OH})_2\text{NO}_3$ as; $a = 6.265 \text{ \AA}$, $b = 3.646 \text{ \AA}$, $c = 7.727 \text{ \AA}$ and $\beta = 96.25^\circ$. The $\text{La}(\text{OH})_2\text{NO}_3 \cdot \text{H}_2\text{O}$ structure consists of lanthanum hydroxide layers in which La^{3+} is 9-coordinate with the interlayer nitrate anions attached directly to the metal in an approximately perpendicular orientation.⁷⁹

Layered rare-earth hydroxides (LRHs) consist of cationic rare-earth hydroxide layers and offer the prospect of combining the optical and catalytic properties of the rare earth elements with the flexibility of intercalation materials. Materials with the composition $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Y, Yb}$)^{78, 80, 81} have been described. Haschke reports an orthorhombic unit cell with $a \sim 6.0 \text{ \AA}$, $b \sim 3.8 \text{ \AA}$ and $c \sim 8.5 \text{ \AA}$.⁷⁸ In the comprehensive study of the preparation of lanthanide hydroxide nitrates Hashke also revealed several related, non-stoichiometric phases with the compositions including $\text{Ln}_2(\text{OH})_{5.14}(\text{NO}_3)_{0.86}$ ($\text{Ln} = \text{La, Pr}$ and Nd) and $\text{Ln}_2(\text{OH})_{5.39}(\text{NO}_3)_{0.61}$ ($\text{Ln} = \text{Sm} - \text{Dy, Yb}$). The preparation of $[\text{Ln}_4(\text{OH})_{10}(\text{H}_2\text{O})_4]\text{A}$ ($\text{Ln} = \text{Y, Dy, Ho, Yb}$; $\text{A} = 2,6\text{-naphthalenedisulfonate, 2,6-anthraquinonedisulfonate}$) phases was reported by Gándara *et al.*⁸² Single crystal diffraction studies revealed an orthorhombic structure for the Y-2,6-naphthalenedisulfonate (YNDS), shown in Figure 10 and Yb-2,6-

anthraquinonedisulfonate (YbAQDS) materials. In these materials the positively charged $[\text{Ln}_4(\text{OH})_{10}(\text{H}_2\text{O})_4]^{2+}$ layers contain lanthanide cations which are 8- and 9-coordinated to μ_3 -hydroxy groups and one water atom giving rise to two different polyhedra; a dodecahedron and a monocapped square antiprism. The organic anions are located between the layers and are ordered through hydrogen bonding interactions with the layers.

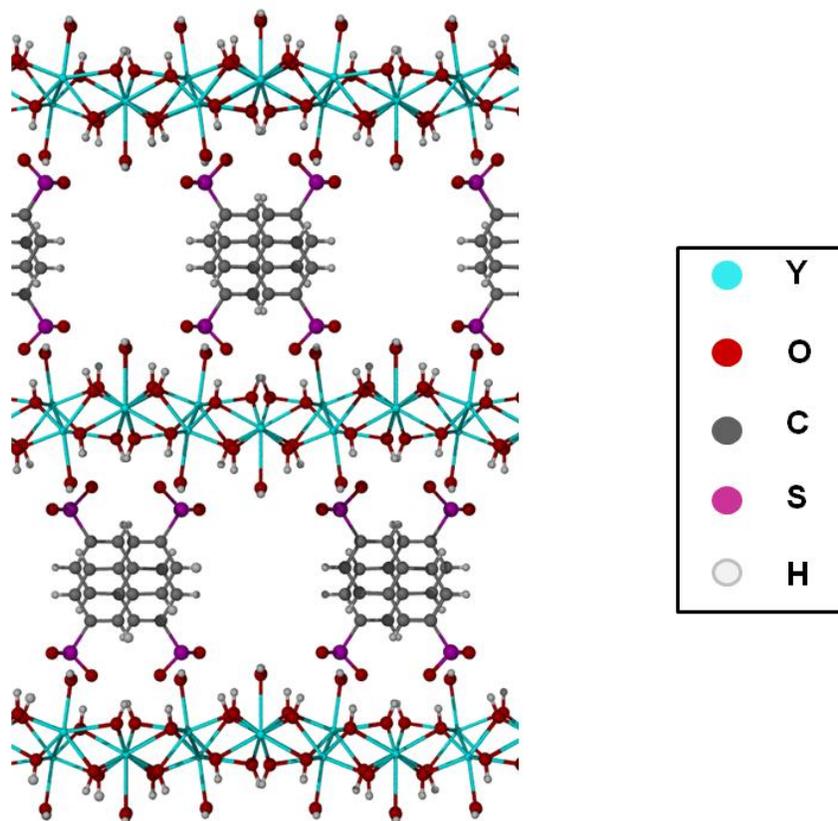


Figure 10 Crystal structure of (a) Y-2,6-naphthalenedisulfonate (YNDS).

1.4 Synthesis

A number of methods can be employed in the synthesis of layered hydroxides, including coprecipitation, ion-exchange, reconstruction through the use of the “memory effect” and hydrothermal methods. As previously noted, LDHs are the most studied family within the layered hydroxides and consequently most of the literature is devoted them. However there are examples of HDS synthesis under ambient conditions and the preparation of hydroxy nitrate salts and LRHs via hydrothermal routes.

1.4.1 Layered Double Hydroxides (LDHs)

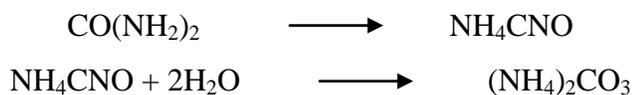
The different routes to LDHs have been reviewed comprehensively.^{50, 55, 83, 84} The most common method of synthesis is coprecipitation, as a “one-pot” method that is readily amenable for scaling-up procedures. It involves the slow addition of a solution of the two metals into water, with simultaneous addition of an alkaline solution in order to maintain constant pH at a level which will facilitate precipitation. The mechanism of layer formation is based on the condensation of $[M(H_2O)_6]^{n+}$ to build brucite layers with distribution of both metal cations and solvated anions.

A number of reaction conditions are thought to be significant for co-precipitation, including temperature, pH, metal ion concentration, concentration of basic solution, flow rate of reactants and ageing time.^{50, 83, 85, 86} Through the careful control of reaction conditions specific anions can be selectively incorporated. The interlayer anions are typically the counter anions of the metal salts although competition between anionic species present can occur. At high pH levels OH^- from the solution can intercalate and where Na_2CO_3 and K_2CO_3 solutions are used CO_3^{2-} is preferentially intercalated. It is also for this reason that many LDH syntheses operate under CO_2 -free conditions at high pH. Avoidance of carbonate contamination is important as CO_3^{2-} is difficult to remove once it has been intercalated. pH range is also very important given that it must be chosen in order that the range of anion stability coincides with the domain of LDH formation.⁸⁷

Water content is dependent on anion size, nature and concentration, external water partial pressure and the washing and drying procedure employed. Water content is particularly significant as it can reversibly or irreversibly affect the host lattice properties, with any changes reflected in the material composition. Thermal treatment can be employed as a means of improving crystallinity of materials synthesised through coprecipitation.⁵⁰

Urea can be used in the synthesis of LDHs. As a weak Brønsted base with $pK_b = 13.8$, it is highly soluble in water and its hydrolysis rate can be controlled by the reaction

temperature. As such it is attractive as an agent for precipitation from homogeneous solution. The hydrolysis of urea proceeds as shown below:⁸⁸



As the temperature is increased from 60 to 100 °C, the rate constant for the reaction increases by up to 200 times. In addition to these key attributes, hydrolysis of urea gives a resulting pH of around 9 and therefore is useful for the precipitation of a great number of hydroxides. Costantino *et al.* have used this route to synthesise $[\text{M}^{2+}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}[(\text{CO}_3)_{x/2}]^{x-} \cdot m\text{H}_2\text{O}$ with $\text{M}^{2+} = \text{Mg}^{2+}, \text{Ni}^{2+}$ and Zn^{2+} .⁸⁹

Calcination of LDHs at moderate temperatures (up to 400 °C) leads to the formation of a poorly crystalline mixed metal oxide through removal of interlayer water molecules and anions and dehydroxylation of the layers. Remarkably, the materials recover their layer structure upon immersion in an aqueous solution of anions and the incorporation of these anions into the interlayer space in a phenomenon known as the “memory-effect”.⁹⁰⁻⁹²

Delamination of LDHs intercalated with surfactants subsequently immersed in butanol has been found by Adachi-Pagano *et al.* to be an effective method by which to prepare LDH/polymer nanocomposites.^{93, 94}

Synthesis via a hydrothermal route generally provides the most crystalline products, although the temperatures need to be chosen carefully in order to prevent the decomposition of the LDH. The two modes of operation for this synthesis are the sealing of an aqueous solution of the LDH precursors in a stainless steel autoclave to facilitate the formation of the product under autogeneous pressure (Figure 11).⁹⁵ The other is to heat a sample in a sealed gold or silver tube at high pressures and temperatures. The hydrothermal reaction of MgO and Al₂O₃ slurries have been investigated from a mechanistic and kinetic viewpoint.^{96, 97} More recently both the urea method and hydrothermal methods have been used in synergy to give MgAl-CO₃ LDH.⁹⁸

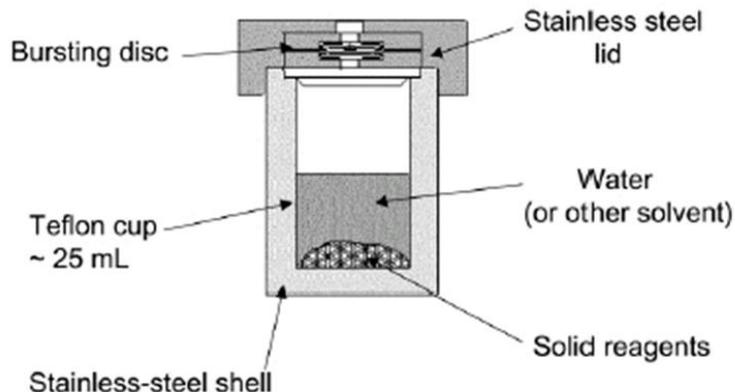
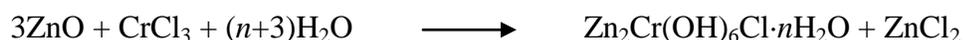


Figure 11 Teflon-lined stainless steel bomb used for hydrothermal synthesis.⁹⁹

Other methods include induced hydrolysis and the salt-oxide method. Induced hydrolysis occurs through a two-step process, the first in the presence of an alkaline solution gives the precipitation of the trivalent metal cation and the hydroxide. The second step involves the slow addition of the divalent cation at constant pH. The salt-oxide method, was first used for the formation of ZnCrCl LDH¹⁰⁰ from the reaction:



The reaction proceeds through the acidic hydrolysis of Zn during CrCl₃ addition and then the coprecipitation of the Zn/Cr hydroxide and is favoured in the pH range 4-7.

More recently the layered hydroxides Co(OH)_{1.65}Br_{0.35}·0.5H₂O, Co(OH)_{1.60}(DDS)_{0.36}Cl_{0.04}·2.1H₂O (DDS = dodecyl sulfate), Mg₂Al(OH)₆NO₃·3H₂O and Mg(OH)₂ have been synthesised by room temperature, controlled ammonia vapour diffusion.¹⁰¹ In this method aqueous metal salt solutions and dilute ammonium hydroxide are left to stand at reduced pressure (approximately 50 mTorr). The materials display unique plate, coral-like and sheet morphologies which can be considered to result from slow crystallisation, with reactions of the order of 10 days.

1.4.2 Hydroxy Double Salts (HDSs)

Typically Hydroxy Double Salts $(M^{2+}N^{2+})_5(OH)_8(A^{n-})_{2/n}$ or $[(M^{2+}_{1-x}N^{2+}_{1+x})(OH)_{3(1-y)/n}]^+A^{n-}_{(1+3y)/n} \cdot zH_2O$ are synthesised from a metal oxide and aqueous metal solutions, the reaction of CuO with Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Mg^{2+} salt solutions have been described.¹⁰² It was via this method that the synthesis of Zn/Co, Zn/Ni, Zn/Cu, Cu/Ni, Ni/Cu, Cu/Zn, Cu/Co and Cu/Cu HDSs was achieved.⁶⁷ Exchange of the interlayer nitrate was complete for organic carboxylates, sulfates and sulfonates, but the materials were notably less reactive towards short chain carboxylates than their LDH counterparts. Copper hydroxy double salts, $Cu_4(OH)_6Br_2$ and the minerals $Cu_2(OH)_2CO_3$, $Cu_4(OH)_6SO_4$, $Cu_4(OH)_6Cl_2$; (malachite, brochantite and paratacamite respectively) can be prepared by reactions of aqueous solutions of the Cu^{2+} salt ($CuBr_2$, $CuSO_4$, $CuCl_2$) with NaOH or Na_2CO_3 solutions.¹⁰³

A one-step route to hydroxy double salt materials with an organic counteranion between the layers has been described.¹⁰⁴ The materials are obtained by room temperature stirring of the metal oxide and metal organic salt in water. Increased crystallinity over the materials obtained by anion exchange is observed. Syntheses with Zn and a range of aliphatic and aromatic carboxylates was achieved where Cu and Ni analogues were not successful.

Anion exchange reactions have been shown to be successful for oxovanadates into Ni, Zn hydroxyacetate by anion exchange at room temperature and at 60 °C followed by hydrothermal treatment at 90 °C and hydrothermal treatment alone at 90 °C.¹⁰⁵ Anion exchange reactions of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ with metal chloride solutions have been reported by Stahlin and Oswald.⁷⁰ Reactions with mono and dicarboxylates proceed upon heated stirring with excess organic.^{79, 106, 107}

1.4.3 Hydroxy Nitrate Salts and Layered Rare Earth Hydroxides (LRHs)

Layered hydroxide nitrates $Cu_2(OH)_3NO_3$ and $Ni_2(OH)_3NO_3$ and have been prepared via precipitation of the metal nitrate solution with sodium hydroxide.⁷⁹ Anion-exchange reactions with the organic anions acetate, terephthalate, and benzoate were attempted at

room temperature, with stirring for 24 hours. Reactions with $\text{Cu}_2(\text{OH})_3\text{NO}_3$ afforded the intercalated materials (with a small amount of unexchanged nitrate still present by elemental analysis) however, with $\text{Ni}_2(\text{OH})_3\text{NO}_3$ exchange reactions were unsuccessful. This observation is attributed to the strong coordination of the interlayer nitrate to Ni^{2+} . $\text{Cu}_2(\text{OH})_3(\text{C}_n\text{H}_{2n+1}\text{SO}_3)$ ($n = 6, 8, 10$) and $\text{Cu}_2(\text{OH})_3(\text{O}_3\text{SC}_4\text{H}_8\text{SO}_3)_{1/2}$ are afforded by anion exchange reactions of $\text{Cu}_2(\text{OH})_3\text{NO}_3$ with sulfonate sodium salts at room temperature.^{108, 109}

$\text{Mg}_2(\text{OH})_3\text{NO}_3$ is prepared by the addition of magnesium nitrate and sodium hydroxide with the precipitate treated hydrothermally at 150 °C for 96 hours. Here it was noted that the formation of $\text{Mg}(\text{OH})_2$ from the hydrolysis of unstable metal hydroxide nitrates was circumvented by an increased nitrate concentration.¹¹⁰ A study by Biswick *et al.* reports the synthesis of a further member of the hydroxynitrate family, $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ and the anion exchange reactions of this material as well as $\text{Mg}_2(\text{OH})_3\text{NO}_3$. The Zn material undergoes anion exchange with benzoate at room temperature however, under the same reaction conditions, $\text{Mg}_2(\text{OH})_3\text{NO}_3$ hydrolyses to yield poorly crystalline brucite.¹¹¹

$\text{La}(\text{OH})_2\text{NO}_3 \cdot \text{H}_2\text{O}$ was prepared by the dropwise addition of NaOH to $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ whilst stirring, followed by hydrothermal treatment at 150 °C for 18 hours.^{79, 112} Successful anion exchange reactions with acetate, benzoate and terephthalate were carried out at 65 °C for 7 days, as shorter reaction times did not give complete exchange and those at room temperature did not proceed at all. Possible reasons for this include coordination of the interlayer nitrate to the metal cation (as for $\text{Ni}_2(\text{OH})_3\text{NO}_3$) but the authors suggest that the severe treatment required in fact suggests a dissolution-reprecipitation mechanism, instead of direct anion exchange. Of the other larger lanthanides that are known to form layered hydroxynitrates with the general formula $\text{Ln}(\text{OH})_2\text{NO}_3 \cdot x\text{H}_2\text{O}$, microcrystalline $\text{Nd}(\text{OH})_2\text{NO}_3 \cdot \text{H}_2\text{O}$ is synthesised by the slow hydrolysis of neodymium nitrate and ammonium nitrate.⁷⁴ As expected, increased crystallinity is gained through hydrothermal routes, with single crystals of $\text{Nd}(\text{OH})_2\text{NO}_3$, $\text{Gd}(\text{OH})_2\text{NO}_3$ and $\text{Pr}(\text{OH})_2\text{NO}_3$ reported.^{76, 77}

There are limited reports into layered rare earth hydroxides (LRHs) with some simply reported as by-products of different investigations. A phase equilibria study of

lanthanide hydroxide nitrates by Haschke yielded phases with the composition $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Yb}$ and Y) from a hydrothermal synthesis.⁷⁸ Schildermans *et al.* reported the room temperature precipitation of $\text{Y}_2(\text{OH})_5\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ during research into the production of a precursor for the synthesis of the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.⁸¹ $[\text{Ln}_4(\text{OH})_{10}(\text{H}_2\text{O})_4]\text{A}$ ($\text{Ln} = \text{Y}, \text{Dy}, \text{Ho}, \text{Yb}$; $\text{A} = 2,6\text{-naphthalenedisulfonate}, 2,6\text{-anthraquinonedisulfonate}$) are synthesised hydrothermally at 180 °C and YbAQDS and YNDS materials yield single crystals.⁸²

1.5 Anion Exchange

LDHs are regarded as the principal class of anion exchangers.¹¹³ There are many methods by which intercalation can be achieved, including direct synthesis, swelling, flocculation and reflocculation and electrointercalation.^{114, 115}

Anion exchange is governed by a number of factors including, anion size, anion orientation, host-guest interactions, degree of hydration and charge density of the layer. Anion exchange provides a means by which the intercalated anion can be exchanged for a different guest species. Reactions are generally facile and result from placing the host materials into a concentrated solution of a guest. A simple schematic to outline the exchange of anions within a lamellar material is shown in Figure 12.

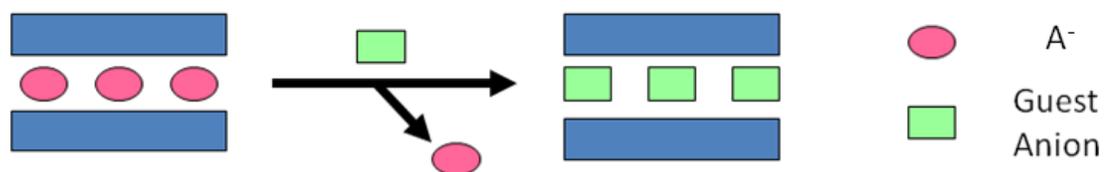


Figure 12 Schematic representation of an anion exchange reaction.

Radha *et al.* postulated that anion exchange reactions take place by one of two mechanisms, (i) by the previously described single-step topotactic mechanism or, (ii) through a dissolution-reprecipitation route.¹¹⁶ The former involving the exchange of anions in a single step leaving the hydroxide layer of the host material relatively

undisturbed and the latter involving delamination to give positively charged hydroxide layers and free anions in solution followed by layer re-stacking to include the guest anion, leaving the host anion in solution. The weak interactions between the metal hydroxide layers and the interlayer anions mean that A^{n-} are readily exchanged and can vary hugely, to include a range of simple inorganic anions, oxoanions, oxometallates, complexes and organics.¹¹⁷ It is well known that the interlayer structure for these materials is difficult to characterise.

1.5.1 Intercalation of Simple Inorganic Anions

Miyata has measured the ion-exchange isotherms for a range of anions intercalating into Mg-Al LDHs and states that the selectivity for monovalent anions is $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ and for divalent anions $CO_3^{2-} > C_{10}H_4N_2O_8S^{2-} > SO_4^{2-}$.¹¹⁸ Divalent anions are selectively intercalated in preference to the monovalent. With this in mind, it is preferential to design materials with monovalent anions, such as NO_3^- in the interlayer space as they are most easily displaced in anion exchange reactions.

In the simplest case, anion exchange is achieved by stirring an aqueous solution of the LDH precursor with a large excess of the anion salt. LDHs containing carbonate anions within the host material are less susceptible to anion exchange reactions due to high selectivity for this anion and so a process such as calcination followed by rehydration is needed to increase the sorption capability of these LDHs.¹¹⁹

1.5.2 Intercalation of Complexes

The intercalation of large anions is an area of interest as the products have applications in adsorption and catalysis. The intercalation of large anions such as cyanocomplexes, oxocomplexes and macrocyclic ligand containing complexes into LDHs and other layered materials has been reviewed comprehensively by Rives and Ulibarri.¹¹⁷

Intercalation of transition metal complexes into a variety of LDHs has been achieved, by Carrado *et al.* and Chisem and Jones.^{120, 121}

Yun and Pinnavaia have demonstrated the intercalation of LDHs with large polyoxometallate (POM) anions.¹²² They were able to successfully intercalate the Keggin anion $(\text{H}_2\text{W}_{12}\text{O}_{40})^{6-}$ and other related anions such as Dawson $(\text{P}_2\text{W}_{18}\text{O}_{62})^{6-}$ and Finke $(\text{CO}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2)^{10-}$ into a $\text{Mg}_2\text{Al}-\text{CO}_3$ LDH. The diameter of these polyoxometallate anions is large; Keggin (~ 10 Å), Dawson (~ 14.5 Å) and Finke (~ 13 Å) compared to that of the interlayer spacing of a LDH, (~ 4.8 Å) and so exchange reactions were attempted by three different routes.

In the first method $\text{Mg}_2\text{Al}-\text{CO}_3$ is calcined to give the corresponding metal oxide which then forms the intercalate upon addition to the POM solution. The second method proceeds via an intermediate adipate intercalate and the third by direct intercalation at pH 4.5. The greatest yield was obtained from the adipate intermediate route, attributed to the use of the organic as a gallery expanding agent. An increase of reaction temperature also resulted in improved product crystallinity.

1.5.3 Intercalation of Organic Anions

Intercalation of the first organic anion, acetate, into a LDH was accomplished by Miyata and Kumura in 1973.⁵⁷ Since this time many organic anions have been successfully intercalated into a range of LDHs. There is much research into this area as LDHs and other layered materials intercalated with organic anions are readily used in a range of diverse applications in industry, these will be described in section 1.6.

Intercalation of carboxylate and sulfonate anions into layered materials has been extensively investigated, Williams *et al.* have intercalated carboxylates and sulfonates into $[\text{MAl}_4(\text{OH})_{12}]\text{NO}_3 \cdot y\text{H}_2\text{O}$ ($\text{M} = \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$).¹²³ Carboxylates were found generally to react faster than sulfonates. The basal spacing of the intercalate was dependent upon the orientation of carboxylates, with the most favourable arrangement found to be with the end of the carboxylate chain oriented toward the positively charged layers. An extensive study by Meyn *et al.* afforded a variety of nitrate LDHs; ZnCr, ZnAl, MgAl, CaAl, LiAl all exchanged with benzoate.³² In this study intercalation was successful in all of the LDHs, with the exception of CaAl- NO_3 LDH in which no reaction occurred.

Polymer-LDH nanocomposites are formed by the intercalation of polymers into LDHs though relatively few literature examples exist. However Orihaki *et al.* have shown that the intercalation of poly(acrylic acid), poly(vinylsulfonate) and poly(styrenesulfonate) into MAI-CO₃ LDHs, (M = Mg²⁺, Ca²⁺ or Zn²⁺) is possible.¹²⁴ It was found that the substituents intercalated with an orientation that maximized electrostatic attractions as shown in the schematic diagram below (Figure 13).

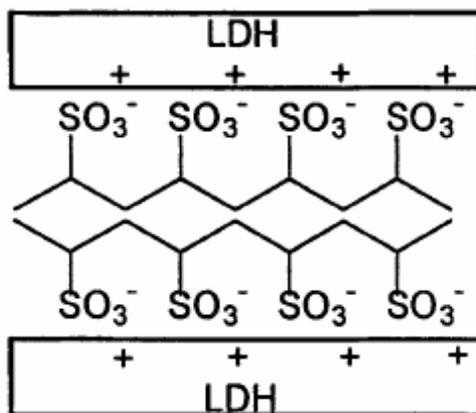


Figure 13 Schematic diagram showing bilayer packing of poly(vinylsulfonate) in the LDH interlayer space.¹²⁴

1.6 Applications of Layered Hydroxides

Layered hydroxides are a hugely versatile class of materials, with their properties tunable by varying the M²⁺ / M³⁺ layer composition and the interlayer anion. The materials are easily synthesised at low cost making them attractive candidates for industrial applications. These applications have been the subject of many reviews in recent years and cover the wide-ranging fields of catalysis, separation science, polymer additives, biological storage and delivery, as well as electrochemistry and photochemistry.^{31, 115, 123, 125}

1.6.1 Catalysis

The cations in the brucite-like layers of LDHs are evenly-distributed and so in principle catalytic activity can be finely tuned according to which metals are used and their ratio within the layer structure. The catalytic properties of LDHs and their applications as catalyst supports, catalyst precursors or actual catalysts are well known and have been reviewed.^{126, 127} LDHs have been reported as catalysts in base-catalyzed reactions, hydrocarbon reformation, hydrogenation, oxidation and as supports for Ziegler-Natta catalysts.⁸⁷ Mixed metal oxides obtained by controlled thermal decomposition of LDHs are known to be highly active catalysts, with large specific surface areas, basic properties and, like pristine LDHs, a homogeneous dispersion of metal ions within the layers. The “memory effect” of these materials also allows the possibility of reconstruction of the layered structure under mild conditions.

The application of LDHs and pillared LDHs as catalysts has been comprehensively reviewed by Braterman *et al.*¹²⁸ LDHs are utilized as catalysts in oxidation reactions due to the ability to catalyze reactions using cheap and non-polluting oxidants such as peroxides and atmospheric oxygen. It is thought that normally unstable oxidation states of metals in solution, such as Cu^{3+} and Mn^{3+} are stabilized in the highly basic environments of the LDH. CuMAl-CO_3 LDHs ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$ and Fe^{2+}) have been used in the hydroxylation of phenol to diphenol in the presence of H_2O_2 .¹²⁹ The oxidation of toluene to benzaldehyde is catalyzed by MgMnAl-LDH ,¹³⁰ similar reactions are also facilitated by CuZnAl-LDH ¹³¹ and CoCuAl-LDH .¹³² Pd(II)-LDH mixtures are reported to be more active in the oxidation of alcohols to carbonyls, with atmospheric O_2 as an oxidant.^{133, 134} The oxidation of ketones to esters has been achieved using MgAl-LDH s incorporating transition metals Fe^{2+} , Cu^{2+} and Ni^{2+} .¹³⁵ The epoxidation of α,β -unsaturated ketones by $\text{MgAl-CO}_3\text{-LDH}$ with H_2O_2 has been reported by Fraile *et al.*¹³⁶ LDHs pillared with large polyvalent anions such as polyoxometallates are able to act as acid catalysts, those intercalated with redox active anions, e.g. Cophtalocyaninetetrasulfonate, can be used as oxidation catalysts.¹²⁸

LDHs and their calcination products have been applied to a number of significant organic reactions including the epoxidation of styrene (MgAl-LDH),¹³⁷ Suzuki-Miyaura cross-

coupling reactions (Pd(II) supported on MgAl-LDH),¹³⁸ aldol condensations (MgAl LDH),¹³⁹ Claisen-Schmidt condensation (MgAl-LDH) and Knoevenagel condensations (NiAl-LDH).¹⁴⁰ Calcined-rehydrated MgAl-LDH has demonstrated selective Michael addition reactions.¹⁴¹ Mixed oxides obtained from MgV-LDHs¹⁴² and Ru(III)-containing MgAl-LDHs¹⁴³ and CoAl LDHs¹⁴⁴ have been reported as oxidation catalysts.

LRHs have displayed promising results in applications as heterogeneous catalysts, the primary example being the study by Gandara *et al.*⁸² YbAQDS, ([Yb₄(OH)₁₀(H₂O)₄]AQDS), has been used in the hydrodesulfurization of thiophene, affording a conversion of 50 % in 26 hours to hydrogen sulfide and butane under 7 bar of H₂ at 70 °C (typical conditions are 30–60 bar H₂ at 350–400 °C). This catalyst also proved effective in sulfide oxidation of a range of alkyl phenyl sulfides (100 % conversion in 30 minutes by H₂O₂). Linalool was oxidized to pyranoid and furanoid ethers (ratio 1:1) with >80% conversion over 24 hours by using YNDS ([Y₄(OH)₁₀(H₂O)₄]NDS) as a bifunctional redox–acid catalyst.

1.6.2 Separation Science

Intercalation reactions of lamellar hosts are not usually selective, however LDHs have been found to be effective at separating mixtures of isomeric guest ions, providing possible applications in separation science.¹²⁰ Layered double hydroxides have been reported to exhibit high selectivity between isomeric pairs of organic anions and have been shown to exhibit preferences of up to 100 % dependant on reaction conditions for a range of aliphatic and aromatic dicarboxylates, and sulfonates.^{145, 146} Fogg *et al.* observed that a LiAl₂-Cl LDH selectively intercalates 1,4-benzenedicarboxylate (BDA) with almost 100% selectivity from an equimolar mixture of 1,2-, 1,3- and 1,4-BDA.¹⁴⁵ Equimolar mixtures of fumarate and maleate gave analogous results with 100% selectivity for fumarate. Investigations into selective anion exchange reactions using 1,5- and 2,6-naphthalenedisulfonate (NDS) have shown that it is possible to control selectivity by altering the reaction temperature and the reaction solvent. From an equimolar mixture of 1,5- and 2,6- NDS at 100 °C, LiAl₂-Cl LDH is found to

selectively intercalate 1,5-NDS in a ratio of 98:2. Lowering the temperature changes the selectivity of the LDH, intercalating the 2,6-NDS in a ratio of 73:27. Changing the solvent in this reaction from water to acetonitrile is also found to affect selectivity; at 100 °C, the 1,5- NDS no longer predominates.

The selective intercalation reactions of $[MAl_4(OH)_{12}](NO_3)_2 \cdot yH_2O$ ($M = Zn, Cu, Ni$ and Co) materials have been thoroughly explored.¹⁴⁷ Preferential intercalation is observed for 1,4-benzenedicarboxylate over 1,2-benzenedicarboxylate (BDA), and for 2-naphthalenesulfonate over 1-naphthalenesulfonate. Reaction temperature and solvent were varied and up to 100% selectivity was achieved. The intercalation of 1,5-naphthalenedisulfonate over 2,6-naphthalenedisulfonate was less selective (45% - 90% 1,5-NDS) depending on reaction temperature and choice of solvent system. The isomer intercalated preferentially can be controlled by the reaction conditions, and by appropriate choice of conditions an almost complete separation of a mixture of these isomers is possible.

Millange *et al.* have shown that $[Ca_2Al(OH)_6](NO_3) \cdot 2H_2O$ (Ca_2Al-NO_3) can separate an equimolar mixture of the disodium salts of 1,2 and 1,4-benzenedicarboxylate (BDA).¹⁴⁸ Only the 1,4-BDA anions are intercalated within the LDH with >95% selectivity. Selectivity of anions is governed by thermodynamic factors; less favourable guest anions are de-intercalated and replaced with thermodynamically favoured anions. In this example the kinetic intercalation phase consists of both 1,2-BDA and 1,4-BDA anions. This kinetic phase collapses rapidly and expulsion of the less favoured 1,2-BDA anion occurs. The thermodynamic intercalation phase containing solely 1,4-BDA remains (Figure 14).

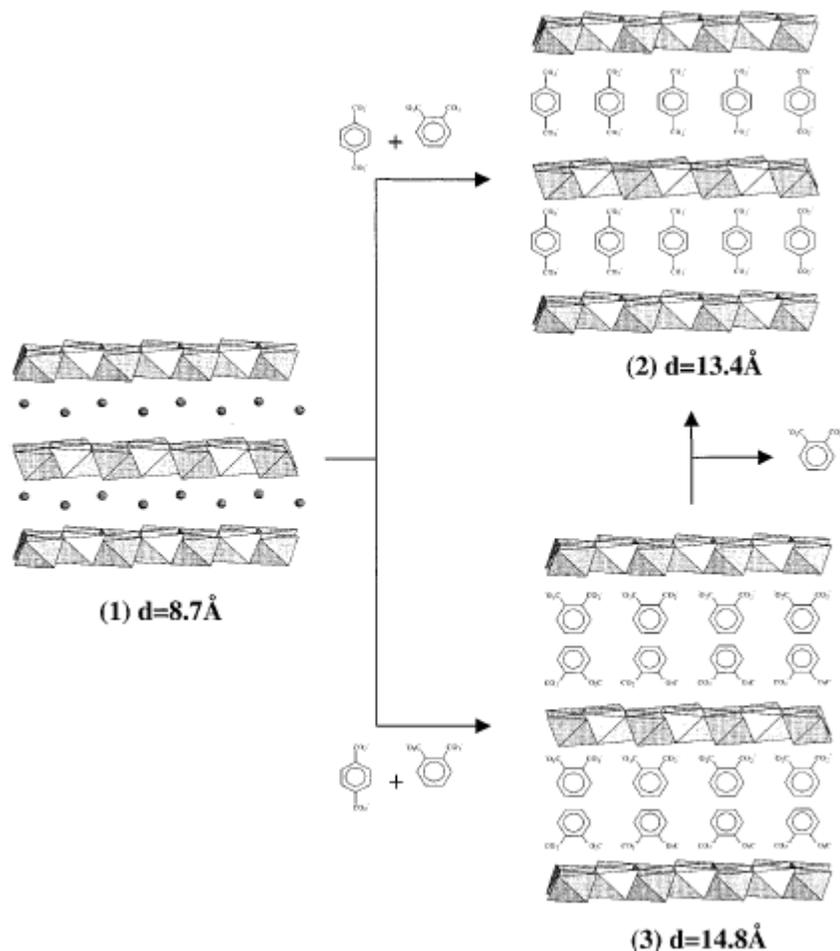


Figure 14 Schematic representation of intercalate phases formed during the competition reaction of 1,2- $\text{C}_8\text{H}_4\text{O}_4$ and 1,4- $\text{C}_8\text{H}_4\text{O}_4$ with $\text{Ca}_2\text{Al}(\text{OH})_6\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (1) to give:
 (2) the thermodynamic $\text{Ca}_2\text{Al}(\text{OH})_6[1,4\text{-C}_8\text{H}_4\text{O}_4]_{0.5} \cdot 4\text{H}_2\text{O}$
 (3) the kinetic $\text{Ca}_2\text{Al}(\text{OH})_6[1,2\text{-C}_8\text{H}_4\text{O}_4]_{0.5} \cdot 4\text{H}_2\text{O}$.¹⁴⁸

1.6.3 Polymer Additives

Poly(vinyl chloride) PVC and other chlorine containing polymers upon exposure to high temperatures or UV radiation undergo autocatalytic dehydrochlorination. Degradation can be curtailed by the irreversible binding of HCl to stabilizers as this species, released during the dehydrochlorination of the polymer, is thought to sustain the catalytic process. The favorability of the heavy metal compounds previously used, such as cadmium or lead stearates, has diminished in the light of concerns over their environmental impact. The largest current application for LDHs in industry is in the

stabilization of PVC.¹⁴⁹ The first report of the use of LDHs for this purpose appeared in 1981 in a patent from Kyowa Chemical Industries and then later in 2000.¹⁵⁰ A later report in 2000 by van der Ven *et al.* suggests that the mechanism by which LDHs react with HCl is a two-step one; firstly, the interlayer anions react with HCl gas followed by the reaction of the LDH layers with HCl resulting in decomposition of the host material, forming the corresponding metal chlorides.¹⁵¹ The investigation involving MgAl LDHs showed that thermal stability was dependent on the identity of the interlayer species, Figure 15.

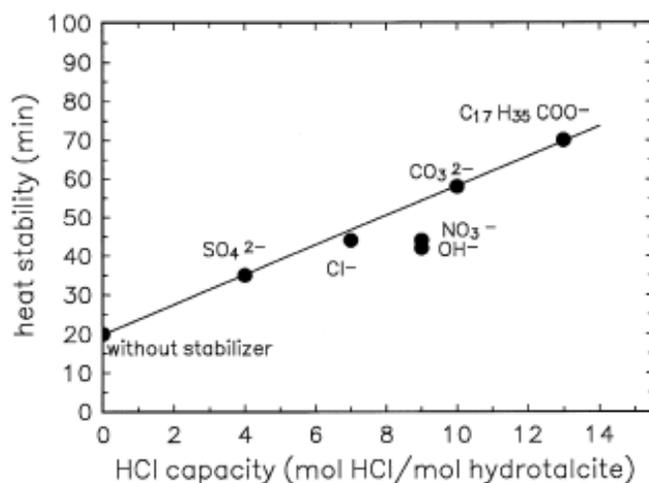


Figure 15 Graph to show the relationship between heat stability and HCl capacity of the MgAl-LDHs with varying counteranion.¹⁵¹

LDHs have also found uses as flame and smoke retardants.¹⁵²⁻¹⁵⁴ Shi *et al.* have shown that the introduction of borate anions into MgAl-CO₃ LDH by reaction with boric acid leads to a significant reduction of smoke during combustion whilst maintaining the flammability properties of the materials.¹⁵⁴

Hydroxy double salts have also been applied as flame retardants in polymers. The thermal degradation of the acetate containing ZCA, ZNA and the layered hydroxide ZHA has been characterised by TGA, DTA and FTIR in order to evaluate the role of metal composition in their effectiveness. It is thought that the structure and composition of the metal hydroxide layer is key.⁷² Indeed the layered basic zinc acetate (LBZA) derivative $Zn_5(OH)_8(CH_3COO)_2(HOC_2H_4OH)_2 \cdot 2H_2O$ formed by intercalation of

ethylene glycol into $Zn_5(OH)_8(CH_3COO)_2 \cdot 2H_2O$ is shown to have high thermal stability. The LBZA film which is formed by chemical bath deposition is immersed in ethylene glycol at room temperature for 48 hours resulting in an increased thermal stability from 130 °C to 180 °C.¹⁵⁵

1.6.4 Biological storage and delivery

LDHs have been identified as suitable candidates for the intercalation and controlled release of biologically-active compounds.¹⁵⁶ The variability of composition is well-reported, hence they can be formulated to ensure bio-compatibility and they are well-known anion-intercalators. The goals and methods of current drug-targeting have been outlined by Gardner.¹⁵⁷ A “targeted-drug” is defined as one which has a high therapeutic index, i.e. it treats a given condition effectively without harming the host and secondly as one in which is directed to a site with little or no effect on other areas of the body. Typically drugs administered in tablet form, are absorbed but activity rapidly drops off, resulting in only a short period where the levels are at their most effective. A future goal is to develop so-called controlled release formulations (CRFs) for the pharmaceutical industry, as a means by which pharmacologically-active levels can be maintained for longer periods, thus reducing potentially harmful side-effects and the requirement for repeat administration. LDHs have been used as biological storage and delivery systems for amino acids^{158, 159}, vitamins^{160, 161}, DNA and other nucleosides^{162, 163} and drug molecules.¹⁶⁴⁻¹⁶⁶ Once intercalated into the LDH, guest molecules are protected from light and oxygen and are released via anion exchange.

A series of pharmaceutically active compounds have been reversibly intercalated into $[LiAl_2(OH)_6]Cl \cdot H_2O$, by Khan *et al.*,¹⁶⁷ including the non-steroidal anti-inflammatory drugs diclofenac, naproxen, tolfenamic acid and ibuprofen, the anti-convulsant and mood-stabilizing drug 2-propylpentanoic acid, 4-biphenylacetic acid (a pharmacologically active metabolite of fenbufen) and the lipid-regulating drug gemfibrozil, see Figure 16. Intercalates were formed upon stirring the LDH in water at 60 °C in a two-fold excess of the drug molecule in the form of its sodium salt. De-intercalation was achieved upon placing the intercalated species into a phosphate buffer

solution at 37 °C at pH 4 and 7. The rate at which the drug de-intercalated was monitored using UV-Vis. The group have also carried out similar experiments with the additional LDHs Mg_2Al-NO_3 and Ca_2Al-NO_3 .¹²³ Results were found to vary considerably according to the host material used, the release times for each LDH are shown in Table 2.

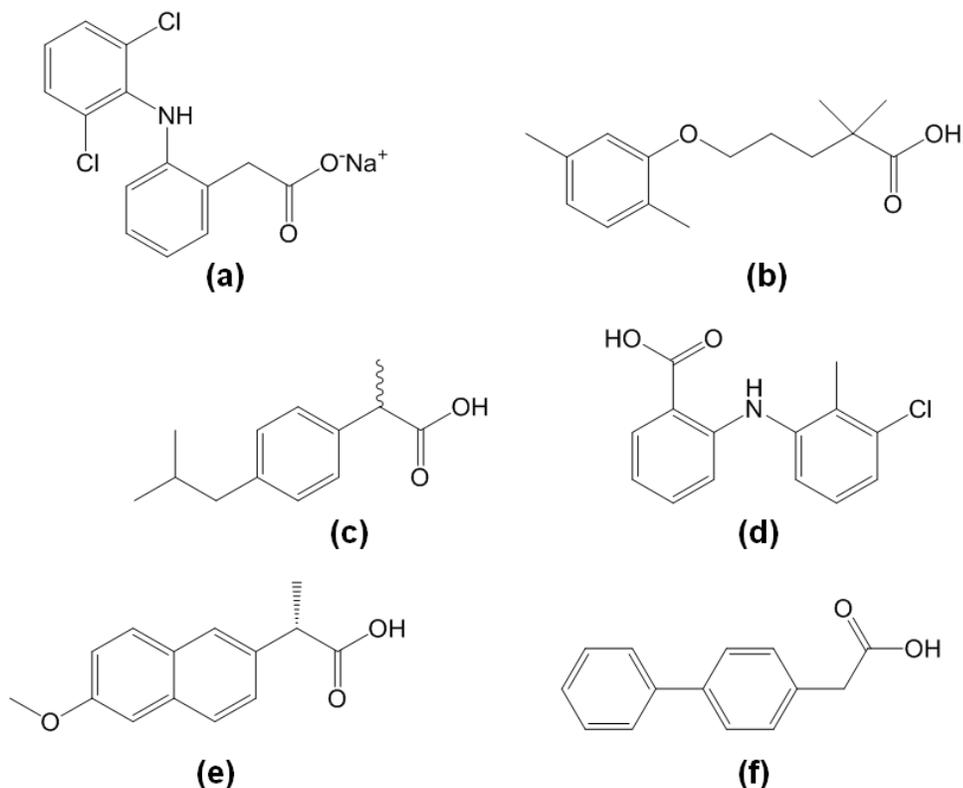


Figure 16 Example of molecules intercalated into LDHs (a) Diclofenac (b) Gemfibrozil (c) Ibuprofen (d) Tolfenamic acid (e) Naproxen (f) 4-Biphenylacetic acid.

However, unmodified LDHs are unsuitable as a means for oral delivery given that the stomach pH = 1.2. For this reason, Duan *et al.* have developed a core-shell material.¹⁶⁸ The fenbufen intercalated LDH was coated by enteric polymers and displayed slow release of the drug molecule under in-vitro conditions.

Table 2 Time taken for 90 % of the intercalated drug to be released at pH 7.5.¹²³

Drug, X	Time (min)		
	Li ₂ Al-X	Mg ₂ Al-X	Ca ₂ Al-X
Diclofenac	4	22	6
Gemfibrozil	5	12	35
Ibuprofen	2.5	13	12
Tolfenamic acid	21	0.5	20
Naproxen	9	2.5	5.5
4-Biphenylacetic acid	2	2	15

Biologically-active molecules are typically chiral and as such, are sensitive to racemisation through heat and light. Clearly protection from such effects is desirable given that enantiomers of the same drug molecule can have vastly different activities and effects. Evans *et al.* have demonstrated that the intercalation of L-tyrosine into NiAl-, MgAl- and ZnAl-LDHs via coprecipitation prevents racemization by heat, light and UV.^{169, 170} Intercalation of the unstable chiral drug L-DOPA into MgAl-LDH enhances its chemical and thermal stability due to strong host-guest interactions.¹⁷¹

Choy *et al.* demonstrated the intercalation of Methotrexate (MTX) and folic acid into MgAl-NO₃ LDH.¹⁷² Folic acid is used in cancer treatment and prevention and for treating vitamin deficiencies whilst MTX, a folic acid antagonist, is also a well known anti-cancer drug. The efficiency of the MTX-LDH hybrid was tested through the use of a bioassay with a tumor cell. No deterioration of either the LDH structure or MTX functionality was found to occur and significantly, the hybrid was actually found to be more efficient in the suppression of tumor cells.

Cardoso and co-workers have compared the intercalation of the anionic herbicides 2,4-dichlorophenoxyacetic (2,4-D), 4-Chloro-2-methylphenoxyacetic acid (MCPA) and picloram into MgAl-LDH via a range of methods including anion exchange.¹⁷³ Release profiles for the materials were measured and revealed slow release for the LDH-herbicide hybrids indicating their potential utility as supports for these molecules.

2,4-D has also been intercalated into $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot x\text{H}_2\text{O}$ LDH (LiAl–Cl LDH) by ion-exchange.¹⁷⁴ The study by Ragavan *et al.* also included the herbicides 4-chlorophenoxyacetate (4-CPA) and 2,4,5-trichlorophenoxyacetate (2,4,5-T), the structures of which are shown in Figure 17.¹⁷⁵ The kinetics and mechanism of intercalation were investigated, with the LDH displaying kinetic selectivity of the order 4-CPA > 2,4-D > 2,4,5-T and thermodynamic selectivity of the order 2,4-D > 4-CPA > 2,4,5-T.

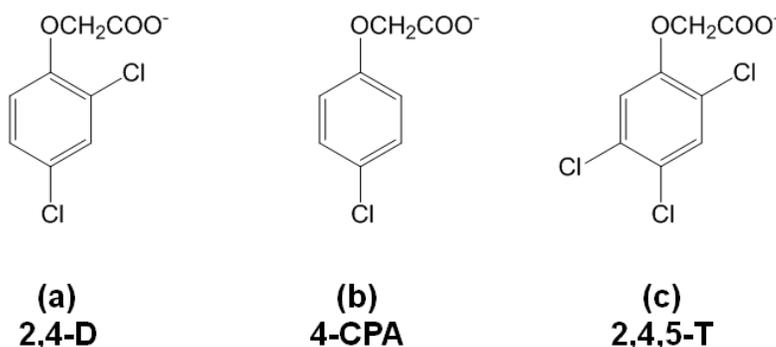


Figure 17 Structures of chlorophenoxyacetate herbicides (a) 2,4-D: 2,4-dichlorophenoxyacetic (b) 4-CPA: 4-chlorophenoxyacetate and (c) 2,4,5-T: 2,4,5-trichlorophenoxyacetate.

1.7 Aims

It has been noted that although the compositional flexibility of layered hydroxides is great, the array of metals incorporated into the host lattice is relatively limited. An area of particular of interest is the rare-earths, known for their optical, catalytic and magnetic properties. It is envisaged that by combining the properties of these metals with the flexibility of lamellar compounds a whole range of potential applications in fields as diverse as optical sensing and catalysis could be further explored.

The primary aim of this thesis is to explore synthetic routes to new layered rare earth hydroxides. The materials will be fully characterised and in this way it is hoped that an increased understanding of their structure and properties will be gained. Similarly, insight into modes of formation would be increased by a study of reaction kinetics. The anion exchange, shape-selectivity and optical properties of the materials will be investigated with the view to expanding the industrial applications of layered hydroxides.

1.8 References

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