Chapter 5
Experimental Details

5.0 Introduction

In this chapter the experimental details and techniques in relation to the work discussed in Chapters Two to Four will be detailed. All of the chemicals were supplied by Aldrich and were used as received without further purification unless otherwise stated.

5.1 Analytical Techniques

5.1.1 Elemental Analysis

Elemental analyses were carried out by Steve Apter in the Department of Chemistry at the University of Liverpool. The metal content of the materials was found by ICP analysis on a Ciros CCD optical emission spectrometer following complete dissolution of the samples in dilute HNO$_3$ and C, H and N analysis was performed on a FlashEA 1112 instrument. Yb$_2$(OH)$_5$NO$_3$·1.5H$_2$O and Yb$_2$(OH)$_5$NO$_3$·H$_2$O analyses were performed by an external company; Elemental Microanalysis Ltd., Okehampton.

5.1.2 Powder X-ray Diffraction

Powder X-ray diffraction patterns were recorded with Cu K$_{\alpha 1}$ radiation of wavelength 1.540598 Å using a Stoe Stadi-P diffractometer operating in Debye-Scherrer geometry (transmission) or Bragg Brentano geometry (reflection). Transmission X-ray diffraction patterns were recorded on samples sealed in either 0.5 mm glass capillaries or on a flat plate spinner, where the sample is sprinkled onto a thin mylar film and secured with a minimal amount of vacuum grease.
In the case of reflection powder X-ray diffraction patterns the samples were mounted on aluminium plates. These have significant Bragg reflections, but the angular location of these does not interfere with sample characterisation.

In the case of samples containing elements which fluoresce in Cu Kα₁ radiation (Eu, Gd, Tb or Dy) powder X-ray diffraction patterns were also recorded using a PANalytical X’Pert Pro diffractometer fitted with a solid state X’Celerator using Co Kα₁ radiation of wavelength 1.7889 Å.

5.1.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measurements were performed using a Seiko SII-TG/DTA 6300 or Perkin Elmer STA 6000 thermal analyser. Approximately 20 mg of sample was mounted in an alumina crucible and heated between 25 and 1000 °C at a rate of 10 °C min⁻¹ under a flow of nitrogen gas.

5.1.4 Transmission Electron Microscopy

Samples for transmission electron microscopy (TEM) analyses were prepared by a fine sample suspension in ethanol before deposition onto a holey carbon grid. Selected area electron diffraction (SAED) patterns were recorded by Dr. Mathieu Allix on a JEOL 2000FX transmission electron microscope equipped with a double tilting goniometer stage (± 30°). EDS measurements were taken using an EDAX inc. Genesis 4000 system with liquid N₂ cooled Si(Li) detector and ultra thin polymer window (UTW).

5.1.5 Scanning Electron Microscopy

Scanning electron micrographs were recorded by Dr. Mathieu Allix or Mr Gary Evans at the Centre for Materials Discovery at the University of Liverpool.

SEM images were recorded using a Hitachi S4800 Type II Cold Field Emission Scanning Electron Microscope. The samples were sputter coated with Au prior to analysis using an Emitech K550X automated sputter coater and were held in place using
a M3 aluminium 15 mm cross-section sample holder. The samples were observed using a mix of upper and lower secondary electron detectors operating at an acceleration voltage of 3 kV with working distance of 8.0 mm. The exact operation conditions are noted on each SEM image.

5.1.6 Fourier Transform Infrared Spectroscopy

Fourier transform infra red (FTIR) spectra were obtained using either a Nicolet Nexus FT-IR spectrophotometer or Perkin Elmer Spectrum 100 FTIR spectrophotometer fitted with the Spectrum 100 Universal Diamond/ZnSe ATR. Where samples were analysed using the Nicolet Nexus apparatus, samples were mixed with KBr prior to recording the spectra. Spectra were recorded between 4000 and 650 cm\(^{-1}\), with 16 scans at a resolution of 4 cm\(^{-1}\).

5.1.7 Solution NMR Spectroscopy

\(^1\)H NMR (400 MHz) spectra were recorded on a Bruker Avance-400 fitted with an automatic sample changer. The solvent used was D\(_2\)O and proton chemical shifts are given relative to TSP (\(\delta = 0\)).

5.1.8 Ultraviolet-Visible Spectroscopy

UV-vis spectra were recorded on solid samples using a Perkin Elmer Lambda 650S UV/Vis Spectrometer in the range 900 - 190 nm.

5.1.9 Fluorescence Spectroscopy

Fluorescence measurements were taken on solid samples using a Perkin Elmer LS55 Fluorescence Spectrometer.
5.2 Synchrotron Radiation Studies

5.2.1 In situ Energy Dispersive X-ray Diffraction

The salient features of the synchrotron radiation source at the U.K. SRS Daresbury Laboratory, Cheshire and the apparatus used for in situ time resolved energy dispersive X-ray diffraction studies on Station 16.4 are described in section 3.2. Further details of the Station design and the energy dispersive technique can be located elsewhere.\textsuperscript{1-4} Figure 1 demonstrates the overall setup of the station, reaction vessels are placed in to the four cell carousel. Each cell is fitted with a furnace and magnetic stirrer, allowing individual heat control and stirring.

![Figure 1 Station 16.4 experimental setup.](image)

Station 16.4 receives radiation from a wiggler magnet operating at a peak field of 6 T. Incident radiation is passed through a water cooled tungsten carbide block to reduce heating by the X-ray beam. Subsequently the beam passes through a safety shutter and mask system and a pinhole rack in order to define the profile of the beam. The rack
comprises a series of holes in a tungsten carbide strip with diameters ranging from 0.05-2 mm. The remote-controlled strip is driven by the computer according to hole to be aligned to the beam. This section and the following tube are evacuated in order to minimise beam scattering and finally the beam passes on to the sample, with usable X-ray flux falling in the range 5 - 120 keV.

Samples are placed in a reaction cell, full details of which are given in section 3.2. A series of parallel molybdenum 25 x 500 mm slits, 0.1 mm thickness, 0.1 mm separation collimate the diffracted beam. A high purity germanium crystal is the main component of the EG&G ORTEC solid state detector. This crystal, 6 mm diameter and 5 mm thick, measures the number of photons as a function of energy and the data is collated using the program PINCER.

To ensure that maximum diffraction intensity is obtained it is necessary to calibrate the apparatus prior to use. In order to ensure that the diffraction lozenge and the centre of the sample cell are aligned, the rig can be manually moved horizontally on the optical bench to record the changing intensity of the diffraction pattern of gibbsite. Vertically, the height should be set so that the beam passes halfway between the stirrer bar and the top of the sample. To do this, a piece of X-ray sensitive paper is attached to the side of the sample vessel and exposed to the beam, the resulting mark with the aid of a micrometer screw is used to adjust the cell position as required.

A radioactive dial source is used to calibrate the detector using the linear relationship,

\[ E = a + bC \]

Equation 1

By successively exposing the detector to a range of known energies, E and recording the channel, C of highest intensity for each resonance, the calibration constants for the detector a and b can be obtained. For this purpose the Kα and Kβ resonances of Ag, Ba, Cu, Mo, Rb and Tb are used.
Before commencing data collection the relationship between \( d \) and \( \theta \) was measured. Zeolite A was chosen as a standard as it has three intense Bragg reflections of known \( d \)-spacing and the \( E \) values for these reflections recorded. The rearrangement of the relationship,

\[
2d \sin \theta = \frac{hc}{E}
\]

Equation 2

with the insertion fundamental constants,

\[
E = \frac{1}{d} \frac{6.11926}{\sin \theta}
\]

Equation 3

the true value of \( \theta \) to be obtained via a plot of \( E \) against \( 1/d \), where \( E \) is in keV and \( d \) in Å.

Finally, resulting data is converted using the program DLConvert for use in the peak profiling program Xfit. The program calculates the peak areas of the Bragg reflections and these values are then used to calculate the \( \alpha(t) \), the extent of reaction at time, \( t \). The Avrami-Erofe’ev rate law was used to model the experimental data, full details of this are given in section 3.3.

The syntheses were performed on the same laboratory scale as described below, in Teflon lined hydrothermal autoclaves which were heated in a temperature controlled block. In a typical experiment the EDXRD spectra were collected with an acquisition time of 30 s at a fixed detector angle of either 1.75, 1.83 or 1.88 °.
5.2.2 Single Crystal X-ray Diffraction

Single crystal X-ray diffraction data were collected on the microcrystal diffraction facility of Station 9.8 at the UK Synchrotron Radiation Source, STFC Daresbury Laboratory. Crystals were covered in a thin film of perfluoropolyether oil and mounted at the end of a two-stage glass fibre and cooled in an Oxford Instruments nitrogen gas cryostream to 120 K. Data were collected using a Bruker D8 diffractometer operating with an APEXII CCD area-detector. Data collection nominally covered a sphere of reciprocal space in three series of ω-rotation exposure frames with different crystal orientation φ angles.

Structural refinements were carried out by Dr Timothy J. Prior at the University of Hull. Reflection intensities were integrated using standard procedures, allowing for the plane polarized nature of the primary synchrotron beam. Semi-empirical corrections were applied to account for absorption and incident beam decay. Unit cell parameters were refined using all observed reflections in the complete data sets. Structures were solved using routine automatic direct methods. The structures were completed by least squares refinement based on all unique measured $F^2$ values and difference Fourier methods.

5.3 Experimental details for Chapter 2

5.3.1 Synthesis of Ln$_2$(OH)$_5$NO$_3$·xH$_2$O (Ln = Y, Gd-Lu) Phases

The Ln$_2$(OH)$_5$NO$_3$·1.5H$_2$O (Ln = Y, Gd – Lu) phases are synthesised via a hydrothermal route. In a typical reaction 7.5 mL of a 0.44 M Ln(NO$_3$)$_3$·xH$_2$O aqueous solution is added to 2.5 mL of an aqueous solution containing 2.10 M NaOH and 1.44 M NaNO$_3$ and treated hydrothermally at 150 ºC (125 ºC for Y) for 48 hours. The resulting solid was filtered, washed with water and ethanol and allowed to dry in air.
5.3.2 Anion Exchange Reactions

Anion exchange reactions were performed between the Ln$_2$(OH)$_5$NO$_3$·xH$_2$O (Ln = Y, Tb – Tm) phases and an aqueous solution containing a threefold molar excess of a range of (di)sodium salts of organic anions at room temperature. In a typical experiment 75 mg of Ln$_2$(OH)$_5$NO$_3$·xH$_2$O was suspended in 5 mL aqueous solution containing a threefold molar excess of the required anion and stirred at room temperature overnight. The resulting suspension was filtered under vacuum and the isolated solid washed with water and ethanol and dried in air.

The anions investigated were oxalate, malonate, maleate, fumarate, phthalate, terephthalate, oxalate, malonate, succinate, glutarate, suberate, decylsulfonate, dodecylsulfate, 2,6-naphthalenedisulfonate and 2,6-anthraquinonedisulfonate.

5.3.3 Synthesis of Carboxylic Acid Sodium Salts

Where the desired acid salt was not available, it was synthesised by dissolving the required acid in a minimal amount of ethanol and reacted with a two fold molar excess of NaOH and stirred at room temperature for 24 hours. The resulting solid was isolated by filtration and washed with ethanol.

5.3.4 Synthesis of [Ln$_4$(OH)$_{10}$(H$_2$O)$_4$]A$_n$ (Ln = Dy, Er)

The synthesis was carried out according the method outlined by Gándara et al.$^5$ where Ln = Dy and Er and A = 2,6-NDS$^2$, 2,6-AQDS$^2$, phthalate, terephthalate and dodecyl sulfate. Ln(NO$_3$)$_3$·xH$_2$O, A$^2$ and H$_2$O were mixed according to a 4:1:4400 ratio and the pH adjusted to 6.5 with Et$_3$N. The resulting mixture was stirred at room temperature for 20 minutes and treated hydrothermally at 180 °C for 18 h. The resulting solid was washed with water and acetone and dried in air.
Selective Anion Exchange Reactions

Competitive anion exchange reactions were carried out according to the method outlined in 5.3.2. The isomers investigated were maleate and fumarate, and phthalate and terephthalate. In a typical experiment, 75 mg of Er$_2$(OH)$_5$(NO$_3$)$_3$·1.5H$_2$O was suspended in 5 mL of water containing an equimolar three-fold molar excess of the isomeric guests. The suspension was stirred at room temperature overnight. The resulting solid isolated by filtration and washed with water and ethanol and dried in air.

To ascertain the relative amounts of each anion intercalated into the host material, a secondary exchange reaction was performed. The resulting intercalation product was reacted with a three-fold molar excess of Na$_2$CO$_3$ in D$_2$O. The solid was removed by filtration and analysed by powder X-ray diffraction. The filtrate was analysed using $^1$H NMR with TSP as the standard, where the relative integration of the peaks observed allowed the relative amounts of each organic isomer to be determined.

Synthesis of Ln$_2$(OH)$_5$X·1.5H$_2$O (Ln =Y, Dy, Er, Yb; X = Cl, Br) Phases

The Ln$_2$(OH)$_5$X·1.5H$_2$O (Ln =Y, Dy, Er, Yb; X = Cl, Br) phases are synthesised via a hydrothermal route. In a typical reaction 7.5 mL of a 0.44 M Ln(X)$_3$·xH$_2$O aqueous solution is added to 2.5 mL of an aqueous solution containing 2.10 M NaOH and 1.44 M NaX and treated hydrothermally at 150 ºC for 12 hours. The resulting solid was filtered, washed and allowed to dry in air.

Synthesis of Mixed Metal Hydroxides Ln$_a$Lnb$_{1-z}$(OH)$_5$NO$_3$·xH$_2$O (Ln$_a$Lnb$_b$ = Yb/Eu, Yb/Gd and Eu/Er)

The Ln$_a$Lnb$_{1-z}$(OH)$_5$NO$_3$·xH$_2$O (Ln$_a$Lnb$_b$ = Yb/Eu, Yb/Gd, Eu/Er) phases are synthesised via a hydrothermal route according to the desired ratios; 90:10, 80:20, 70:30. For example, the synthesis of Eu$_{1.4}$Er$_{0.6}$(OH)$_5$NO$_3$·xH$_2$O was as follows: 0.23 M Eu(NO$_3$)$_3$·5H$_2$O and
0.10 M Er(NO$_3$)$_3$·5H$_2$O in 7.5 mL of water was added to 2.5 mL of an aqueous solution containing 2.10 M NaOH and 1.44 M NaNO$_3$ and treated hydrothermally at 150 °C for 48 hours. The resulting solid was filtered, washed and allowed to dry in air. Characterisation was carried out by powder X-ray diffraction and EDS.

### 5.4 Experimental details for Chapter 3

#### 5.4.1 In situ EDXRD Experiments

The Ln$_2$(OH)$_5$NO$_3$·xH$_2$O (Ln = Yb, Er, Y) phases investigated are synthesised via a hydrothermal route as outlined in section 5.3.1. In a typical reaction 7.5 mL of a 0.44 M Ln(NO$_3$)$_3$·xH$_2$O aqueous solution is added to 2.5 mL of an aqueous solution containing 2.10 M NaOH and 1.44 M NaNO$_3$ and treated hydrothermally at temperatures ranging from 100 – 240 °C, with constant stirring to ensure sufficient sample remained in the beam. Reaction time varied as the reactions were generally stopped when the required phase was observed. As some of the phases were particularly short-lived, the reactions were quenched by taking them out of the carousel immediately and allowing them to cool. The resulting solid was filtered, washed and allowed to dry in air.

#### 5.4.2 Conditions for Phase Isolation

Phase 1 (Yb$_2$(OD)$_5$NO$_3$·1.5D$_2$O, d = 9.2 Å) was isolated by quenching of a reaction at 175 °C under the standard conditions outlined above. To obtain the deuterated material, Ytterbium nitrate was dehydrated by heating to 100 °C under vacuum and NaOD solution was used in place of NaOH in the hydrothermal reaction.

Single crystals of phase 2 (Yb$_2$(OH)$_5$NO$_3$·2H$_2$O, d = 9.4 Å) were isolated ex situ by increasing the concentration of Yb(NO)$_3$·5H$_2$O to 0.50 M solution. To the solution 2.10 M NaOH and 1.44 M NaNO$_3$ were added and with hydrothermal treatment at 125 °C with slow cooling at 0.1 °C min$^{-1}$.
Phase 3 (Yb$_2$(OD)$_5$NO$_3$·D$_2$O, d = 8.5 Å) was isolated by quenching of a reaction at 210 °C under the standard conditions outlined above, with NaOD and dehydrated Yb(NO$_3$)$_3$.

Phase 4 (Yb$_4$(OH)$_9$NO$_3$, d = 8.0 Å) can be isolated ex situ under standard Yb and hydroxide concentrations with hydrothermal treatment at temperatures in excess of 175 °C.

5.5 Experimental details for Chapter 4

5.5.1 Synthesis of Ln$_2$(OH)$_5$NO$_3$·H$_2$O (Ln = Y, Eu–Er)

The method reported by Brigandi et al. for the synthesis of copper hydroxy double salts was used in an attempt to prepare Ln(OH)$_2$NO$_3$·0.5H$_2$O (Ln = Y, Gd – Lu). The hydroxy nitrate phases, Ln$_2$(OH)$_5$NO$_3$·H$_2$O (Ln = Y, La–Lu), were synthesised by a precipitation route. In a typical experiment, 25 mL of 1 M NaOH was added dropwise on to solid Ln(NO$_3$)$_3$·xH$_2$O (0.016 mol for Ln = Y, Dy, Er, Tm and Y and 0.008 mol for Ln = Eu, Tb and Ho) and stirred at room temperature for 30 minutes. The resulting solid was filtered under vacuum, washed with water and ethanol and left to dry, initially in air for 1 hour, and then dried in an oven at 120 °C for 1 hour.

5.5.2 Anion Exchange Reactions of Ln$_2$(OH)$_5$NO$_3$·H$_2$O (Ln = Y, Eu-Er)

For the anion exchange reactions 75 mg of the host lattice was suspended in 5 mL of an aqueous solution containing a three-fold molar excess of the required anion and stirred at room temperature overnight. The reactions were subsequently filtered under vacuum and the product washed with water and ethanol before being left to dry in air. The anions used in this study were the (di)sodium salts of phthalate, terephthalate, fumarate, maleate, malonate, succinate, suberate, decylsulfate, 1,5-naphthalenedisulfonate (1,5-NDS), 2,6-naphthalenedisulfonate (2,6-NDS) and anthraquiononedisulfonate (AQDS).
5.5.3 Synthesis of Ru doped MgAl LDHs

The precious metal salts RuCl$_3$·xH$_2$O and Pd(NO$_3$)$_2$·xH$_2$O, PdCl$_2$·xH$_2$O and Pd(OAc)$_2$·xH$_2$O used for in the synthetic methods described in this section were supplied by Precious Metals Online (Pty) Ltd and were used as received without further purification.

5.5.3.1 Attempted Hydrothermal Synthesis

In a typical synthesis 7.5 mL of a 0.44 M Pd(NO$_3$)$_2$·xH$_2$O aqueous solution is added to 2.5 mL of an aqueous solution containing 2.10 M NaOH and 1.44 M NaNO$_3$ and treated hydrothermally at 150 ºC for 48 hours. The resulting solid was filtered, washed and allowed to dry in air. Reaction temperatures were varied between 100 – 150 ºC, times between 24 and 48 hours and metal concentrations in the range 0.1 – 0.5 M.

5.5.3.2 Attempted Synthesis by Slow Growth Method

2 mL of a 0.25 M solution of Pd(NO$_3$)$_3$·xH$_2$O was poured into one side of a glass H-Cell. 2.5 mL of solution containing 2.1 M NaOH and 1.44 M NaNO$_3$ was added to the opposite side. Distilled water was then added to raise solution level to bridge, ensuring slow addition to minimize perturbation of the solutions. H-cell was then covered with parafilm and allowed to stand at room temperature for 3 months. The resultant amorphous solid was filtered, washed with water and ethanol and dried in air.

5.5.3.3 Attempted method by Vapour Diffusion Method

Reactions were carried out according to a method reported by Du and O’Hare. In a representative method, one beaker containing a dilute solution of NH$_4$OH (0.3–0.7%) and one containing a solution of 0.1 M RuCl$_3$·xH$_2$O were covered with parafilm. The parafilm was then perforated to allow for slow vapour diffusion. The two beakers were
then placed in a vacuum desiccator evacuated and stored at room temperature for 10 days. The precipitates were isolated with vacuum filtration and washed with water.

5.5.3.4 Coprecipitaion-Urea Method

The method was adapted from the literature preparation of \([\text{Ni}_6\text{Fe}_2(\text{OH})_{16}](\text{CO}_3)\cdot5\text{H}_2\text{O}.\)\(^8\) 0.25 mM trisodium citrate, \(\text{C}_6\text{H}_5\text{Na}_3\text{O}_7\cdot\text{H}_2\text{O}\) (TSC) solution was added to 100 mL aqueous solution of \(\text{Pd(NO}_3)_2\cdot\text{xH}_2\text{O}\) (15 mM), \(\text{Al(NO}_3)_3\cdot9\text{H}_2\text{O}\) (5 mM) and urea (35 mM) and stirred at room temperature. The resulting solution was then treated hydrothermally at 150 °C for 48 hours. The solid product was isolated under vacuum, washed with water and ethanol and dried in air.

5.5.3.5 Coprecipitation Method

The samples were prepared with \(\text{M}^{2+}/\text{M}^{3+}\) ratio of 3 and variable \(\text{Ru}/(\text{Al}+\text{Ru})\) ratios (\(\alpha = 0, 0.25, 0.5, 0.75\) and 1.0) using a coprecipitation method based on that reported by Rousselot et al.\(^7\) A typical synthesis is as follows, \(\text{MgAlRu-Cl}\) was prepared through the dropwise addition of a 50 mL aqueous solution of \(\text{MgCl}_2\cdot\text{xH}_2\text{O}\) (0.75 M), \(\text{AlCl}_3\cdot9\text{H}_2\text{O}\) (0.125 M) and \(\text{RuCl}_3\cdot\text{xH}_2\text{O}\) (0.125 M) to 100 mL water. The solution was maintained at pH 10 via the addition of 2 M NaOH solution and the reaction was carried out 60 °C. Once the addition of the nitrate solution was complete, the reaction was stirred at 60 °C for a further 24 hours. The product (black solid) was isolated by centrifugation and washed with water. The solid was dried in an open air oven for 2.5 hours.

5.6 References


