Layered nickel hydroxide salts: synthesis, characterization and magnetic behaviour in relation to the basal spacing†

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Layered nickel hydroxide salts Ni(OH)2−(A)x·nH2O (A = NO3−, n-alkylsulfonates CH3(CH2)nSO3− with n = 10, 14, 18) have been prepared by exchange reaction in aqueous medium at pH = 8.5, starting from the layered hydroxide acetate Ni(OH)1.6(CH3COO)0.4·nH2O. This parent compound has been synthesized by hydrolysis in polyol medium. The obtained compounds present the typical features of the brucite-like structure with turbostratic disorder and an interlayer spacing varying in the range 7.5–32 Å. The magnetic properties have been investigated by means of dc and ac measurements. Two main interactions are found in these materials. On one hand, ferromagnetic in-plane exchange interactions dominate at high temperature, as deduced from the positive Weiss constant, while interlayer ferromagnetic interactions of dipolar origin are responsible for the 3D order at low temperature. This order is indicated by the hysteresis loops below a critical temperature lying in the range 16–18 K. The magnetic properties will be discussed in relation to the structural features, and are mainly driven by the length of the intercalated anion and its head-group functionality. It will be shown that these compounds form a novel series of layered materials for which the model of ferromagnetic layers interacting through dipolar coupling can be successfully applied.

1. Introduction

Layered double hydroxides [LDHs: (M1−xM2x(OH)2)·(xA−·nH2O)]; also referred to as hydrotalcite-like compounds (HTLs), have provoked much interest over the last two decades because of the versatile properties they show in various fields (catalysis, ion exchange, ... etc.). These properties are mainly related to the structural features of such compounds. Layered double hydroxides are derived from the layered hydroxide M(OH)2 by replacing some of the M2+ ions in O6 sites with trivalent ions (M(III)). The positive charge of the layers is counterbalanced by intercalating anionic species together with water molecules in between the layers. As shown by structural studies, the two intercalated species are randomly located in the interlayer space, and are free to move. The interlayer cohesion is provided by hydrogen bonds between the hydroxyl groups of the inorganic sheets and the intercalated species: anion and water molecules.1,2 The properties of such compounds can be tuned by acting upon two main factors: the nature of the M2+ and M(III) cations, and the size of the A− anion. Indeed, while the in-plane metal–metal distance remains almost constant (~ 3 Å), the interlayer distance may be varied over a large scale, and further the introduction into the layers of paramagnetic cations may lead to interesting magnetic properties.

Using these structural features, several groups have developed new hybrid materials with desired functionality depending mainly on the nature of the intercalated anion A−. Electroactive anions such as 2,2′-azobis(3-ethylbenzothiazoline-6-sulfonate) have been intercalated for electrochemical applications,3 and porphyrin to obtain mineral supports for oxidation reaction by cytochrome P-450.4 More recently several works have been devoted to nanocomposite materials built up from the assembly of organic polymers in the interlayer space of two-dimensional host materials, particularly layered double hydroxides (LDHs).

Another interesting property of these materials is their controllable dimensionality. When a small anion such as carbonate is intercalated, a relatively strong interaction may occur between the layers. In turn, by gradually stepping up the incorporated anions, the lattice dimensionality is expected to be reduced to 2D without any strong interaction between the layers. When the layers are far enough from each other (d > 50 Å), they may be considered as exfoliated.

According to the structural features, these materials appear appropriate for the study of magnetic properties in relation to the lattice dimensionality since the interplanar interactions may be tuned by means of the intercalated anion size. In fact, few works have been devoted to the magnetic properties of these materials, owing to the random distribution of the paramagnetic species which makes the analysis of the data a difficult task.6 In this respect, the layered metal hydroxyl salts M(OH)1−x·A·nH2O (M = Co, Cu, Ni) appeared much more promising, due to (i) the presence of a single metal ion in the O6 sites, (ii) the ability of these compounds to partly exchange the hydroxyl groups for larger anions. In this context, systems with M = Cu and Co have been widely investigated over the past decades.7-11

As regards nickel(II) compounds, the examples in the literature are scarce. Only Ni5(OH)6(NO3)4.8H2O12 and Ni3(OH)2·(C12H24S4O9)·H2O13 have been reported. The hydroxynitrates exhibits metamagnetic behaviour and at low temperature spin-glass features, while the sulfonate exhibits long-range ferromagnetic order below 18 K. In order to discuss the
magnetic behaviour of such compounds in relation to their
dimensionality other nickel(n) hydroxy salts with different
basal spacings are needed. This work reports the synthesis,
chemical and physical characterizations of a series of layered
nickel(n) hydroxy salts (denoted hereafter LHS-Ni) with
basal spacings varying in the range 7.5–32 Å. The magnetic
properties will be discussed and compared to those of the
copper(n) and cobalt(n) analogues.

2. Experimental

2.1. Sample preparation
The hydrated nickel acetate, sodium nitrate, sodium alkylsul-
fonate salts and diethyleneglycol were purchased from Prolabo
and used without any further purification.

2.1.1. LHS-Ni-Ac preparation. The series of nickel(n)
hydroxy salts was synthesized via anionic exchange reaction
starting from the layered nickel(n) hydroxyacetate (LHS-Ni-
Ac). The method to prepare this parent compound was adapted
from that described for the first time by Poul et al.14 It consists
of the hydrolysis at 172 °C of nickel acetate tetrahydrate
dissolved in diethylene glycol (0.1 M). As discussed elsewhere,15
the precipitation of LHS-Ni-Ac occurred, as in the sol–gel
method, via hydrolysis and inorganic polymerisation reactions.

2.1.2. Exchange reaction. In order to lower the amount of
CO$_3$$^-$ in solution and accordingly in the final product as
adsorbed or intercalated species, several precautions were
taken during exchange reactions. First, water was boiled before
use to remove dissolved CO$_2$. Second, exchange reactions were
conducted under bubbling nitrogen throughout the solution.
And third, the final products were dried and then kept in plastic
bottles under nitrogen atmosphere. The exchange reaction
procedure is as follows. 250 ml of 0.012 M of neutral solution
of the sodium salt (nitrate, alkylsulfonate) were prepared.
500 mg of LHS-Ni-Ac were added to these solutions and
dispersed at room temperature. During exchange reactions
conducted at room temperature, the pH increased and reached
8.5 because of the release of acetate anions. The exchange was
conducted under vigorous stirring and was completed after one
day by repeating twice the treatment of the recovered product
with fresh sodium salt solution. The final products were washed
three times with alcohol and then dried under nitrogen at room
temperature.

Oriented films of LHS-Ni-Ac for magnetic anisotropy mea-
surements were prepared according to the following procedure.
The nickel hydroxyacetate was dispersed in ethanol in order to
obtain a colloidal suspension. Upon settling and slow drying at
room temperature the crystallites were deposited onto Kapton,
with a preferential orientation, the layer stacking direction
being perpendicular to the substrate.

2.2. Chemical analysis
Carbon, nitrogen and hydrogen elemental analysis was performed
at the Centre d’analyse de l’Université Pierre et
Marie Curie. Nickel was titrated against EDTA using alcoholic
dithizone as indicator. The amount of acetate in the parent
compound was determined by ionic chromatography with a
DIONEX DX-100 ion chromatograph equipped with AG-4
and AS4-SC columns.

The ratio S/Ni for samples containing alkylsulfonate chains
was estimated by Energy dispersive X-ray spectroscopy using a
Leica Stereoscan 440 microscope.

2.3. Characterization
Powder X-ray diffraction data were collected on a Siemens
D5000 Kevex diffractometer in the range 2–100° (2θ) using Cu-
K$_\alpha$ radiation (λ = 1.5405 Å). The particle size was calculated
using the Debye–Scherrer equation. Electron microscopy and
diffraction studies were conducted on a JEOL-100 CX II
microscope. Differential thermal and thermogravimetric ana-
lyses (DTA and TGA) were carried out on a Setaram TG 92-12
thermal analyser in the temperature range 25–1000 °C with a
heating rate of 1 °C min$^{-1}$ under oxygen, in an alumina
crucible. FT-IR spectra were obtained by transmission on an
Equinox 55 spectrometer on pressed KBr pellets in the range
400–4000 cm$^{-1}$ with 4 cm$^{-1}$ resolution. The magnetic mea-
surements on powdered samples enclosed in a medical cap
were carried out in the temperature range 2 to 300 K using a
commercial SQUID magnetometer “MMPSS–SS” from Quan-
tum Design Corp. Field constant and isothermal de magnetisa-
tion were performed with a field strength of 20 mT and in a field
range of 2–5 T.

3. Results and discussion

3.1. Chemical composition
The exchange has been conducted in a basic medium (pH =
8.5) due the release of acetate during exchange. Whereas IR
and XRD analyses (see discussion below) clearly show that
exchange of acetate anion is complete, chemical analysis reveals
that the ratio N/Ni or S/Ni is lower than the acetate ratio in
the parent compound. In fact, the acetate anions are totally
exchanged by A$^-$ and OH$^-$ in proportion depending on the
nature of A$^-$. The carbon and hydrogen contents in the final
product and TGA, DTA results (Table 1) are in good agree-
ment with this hypothesis. It should be noted that the
intercalated alkylsulfonate content is higher than the nitrate
content because of their more basic character. The chemical
formula was inferred from the nickel, nitrogen and sulfur
contents determined by chemical analysis; the water content
has been deduced from TGA analysis. The as-obtained formula
is in good agreement with experimental carbon and hydrogen
amounts and the total loss deduced from TGA analysis (Table 1).
Nitrate and acetate compound formula are very close to
that previously published$^{14,16–18}$

It should be noted that carbon is still present in LHS-Ni-NO$_3$
(1.8%), this may be due to the adsorption of trace acetate or
polyol not removed during washing rather than intercalated
carbonate anions due to the experimental synthesis conditions
chosen to prevent their presence. Such adsorption of organic

Table 1 Elemental chemical analysis data

<table>
<thead>
<tr>
<th>Sample</th>
<th>A/Ni$^b$</th>
<th>C$^b$</th>
<th>H$^b$</th>
<th>H$_2$O$^c$</th>
<th>Total loss</th>
<th>Molecular formula</th>
</tr>
</thead>
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<tr>
<td>LHS-Ni-Ac</td>
<td>0.51</td>
<td>11.52</td>
<td>10.04</td>
<td>2.36</td>
<td>3.21</td>
<td>6.6</td>
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<td>LHS-Ni-NO$_3$</td>
<td>0.16</td>
<td>1.81</td>
<td>23.1</td>
<td>2.55</td>
<td>2.65</td>
<td>3.52</td>
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<tr>
<td>LHS-Ni-C$_{10}$SO$_3$</td>
<td>0.25</td>
<td>20.21</td>
<td>20.09</td>
<td>5.44</td>
<td>5.10</td>
<td>11.5</td>
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<tr>
<td>LHS-Ni-C$_{14}$SO$_3$</td>
<td>0.30</td>
<td>27.2</td>
<td>26.21</td>
<td>6.4</td>
<td>6.65</td>
<td>5.8</td>
</tr>
</tbody>
</table>

$^a$Molar ratio with A exchanged ion. $^b$Weight percentage from elemental chemical analysis. $^c$Weight percentage from TG analysis.
species has often been observed for inorganic materials prepared in polyol medium. Another argument in favor of the presence of trace acetate or polyol rather than carbonate is the presence of very weak CH3 vibration peaks at around 2900 cm⁻¹. At low frequency, two bands which appear between 1600 and 1380 cm⁻¹ are present. They can be related to the splitting of the ν3 and ν2 vibration mode of NO3⁻ in D3h symmetry. On the other hand, two other bands at 1478 and 1308 cm⁻¹ are present. They can be related to the splitting of the ν3 and ν2 vibration mode of NO3⁻ in C2v symmetry. The D3h symmetry is consistent with free nitrate ions intercalated in the interlayer space as observed in LDH compounds, whereas the C2v symmetry is consistent with nitrate ions linked to nickel cations. Altogether these results show the occurrence of two types of nitrate ions in LHS-Ni-NO3 as previously observed for the similar compound nickel hydroxynitrate. This behaviour has also been observed for carbonate anion in the α- and α′-cobalt nickel hydroxides.

The three samples LHS-Ni-C₆H₄(NO₃)ₓSO₃ (n = 10, 14 and 18) [Fig. 2(a–c)] exhibit sharp peaks at 1047 cm⁻¹ and broader peaks at 1170 cm⁻¹ which are indicative of SO₃⁻ groups and correspond to the νas and νs vibration modes of this anion respectively. The positions of these two bands are almost identical to those observed for sulfonate anions intercalated in LDH compounds. For instance, in LDH-Mg-Al-PSS (polyvinylsulfonate) and LDH-Mg-Al-PSS (polystyrenesulfonate), these bands appear at 1196 and 1037 cm⁻¹ respectively, for porphyrin sulfonate anion intercalated in LDH-Zn-Cr, the two bands appear at 1177 and 1037 cm⁻¹. Furthermore, the difference νas − νs (140 cm⁻¹) obtained here is very close to those of the cited LDH compounds. This clearly shows that, as in LDH compounds, the n-alkylsulfonates are not directly linked to the nickel ion, contrary to the result reported by Kurmoo et al. for the isotypic compound Na₂(OH)(C₂H₅SO₃)·H₂O.

In conclusion, despite their similar formulate and structural features, the LHS-Ni compounds present a significantly different interlayer organization. In LHS-Ni-Ac, the acetate anions replace the missing hydroxyl groups and are therefore coordinated to the metal ions as unidentate ligands. In the case of LHS-Ni-C₆H₄(NO₃)ₓSO₃ (n = 10, 14 and 18), the sulfonate anions are located between the layers and linked to the metal via hydrogen bonds as in LDH compounds. The vacant hydroxyl sites may be occupied by water molecules or remain vacant as it was discussed in several works for the so-called α-Ni(OH)₂ and α-Co(OH)₂ which actually are hydroxysalts with the general formula M(OH)ₓ...(NO₃)ₙ(CO₃)₂⁻·nH₂O (M = Ni, Co and x = y + 2).

The nitrate exhibits intermediate behaviour. In the LHS-Ni-NO₃, this anion is partly coordinated to the nickel ion and located in the vacant hydroxyl sites. However, some hydroxyl sites remain vacant and the corresponding nitrate anions are located between the layers and are only linked to the metal by hydrogen bonds.

3.3. Thermal analysis

Fig. 3 and 4 depict TGA/DTA plots of the LHS-Ni compounds studied here. All the compounds present a first weight loss region (50–160 °C) with broad endothermic peaks in the DTA plots. The corresponding weight loss (3–11 wt%) is due to the departure of surface and intercalated water. A second weight loss (24–53 wt%) is observed in the temperature range 200–450 °C. It corresponds to the intercalated anion decomposition and dehydroxylation of the brucite-like sheets. For LHS-Ni-NO₃, the weight loss is accompanied by an endothermic peak, as is usually observed in LDH decomposition. The other compounds show strong concomitant exothermic peaks hiding the endothermic event usually observed. This exothermic peak is due as suggested by Poul et al. to catalytic oxidation of the carbon organic species caused by the presence of nickel oxide. Such an exothermic event has recently been reported for layered Ni(n)–Zn(s) hydroxycarbonates. For LHS-Ni-alkylsulfonate, a third weight loss (4–11 wt%) with a weak
and broad endothermic peak was observed in the range 650–
800 °C. It may be attributed to the complete oxidative elimina-
tion of carbonaceous residues derived from the pyrolysis of
the initial alkylsulfonate groups. Oriakhi et al. have reported
similar behaviour for LDH-Mg-Al-PSS nanocomposites.

At last, for all the compounds, X-ray diffraction analysis
shows that the final product of thermal decomposition is
NiO. The total loss is in good agreement with the calculated
one inferred from the chemical formula (Table 1).

3.4. X-Ray and morphological characterizations

The powder X-ray diffraction patterns are shown in Fig. 5. All
exhibit typical features of incompletely ordered materials
related to the brucite structure evidenced by strong and sym-
metrical reflections at low 2θ values corresponding to (00l)
planes, and broad and asymmetric reflections lines at high 2θ
values corresponding to the non-basal planes. Such features
can be explained on the basis of a stacking order of brucite-like
sheets parallel and equidistant along the c axis of the hexagonal
cell but twisted against each other. This turbostratic character
has been observed for LHS-M-Ac (M = Zn, Co, Ni),14
α-Ni(OH)2 and α-Co(OH)2,21,26 and several layered double
hydroxides.2,23,24 The turbostratic character is usually related
to a particular morphology: the material appears as aggregates
of thin crumpled sheets without any definite size. Such
morphological characteristics are observed for the products
studied here. Fig. 6 and 7 show as examples the LHS-Ni-NO3
and LHS-Ni-C10SO3 particle morphology. Furthermore, the
electron diffraction pattern of the nitrate confirms the hexa-
gonal symmetry of the brucite structure, to which all the
hydrotalcite-like materials belong, and the preferential orienta-
tion of the crystallites along the (001) plane (Fig. 8).

The interlayer distances and crystallite sizes along the c axis
are reported in Table 2. The basal spacing of the final products
varies between 7.5 and 31.7 Å in relation with the anion size.
In all cases, we did not observe any reflections of the starting
compound, indicating that the total exchange reaction has been
successfully realized.

The crystallite size along the c axis increases from 64 Å to
191 Å as the basal spacing increases from 7.5 Å to 31.7 Å, however the number of layers per crystallite remains almost constant (about 6–9 layers/crystallite) for all the products including the parent compound as expected for a topotactic exchange reaction.

It is interesting to note that, for LHS-Ni-alkylsulfonates, a linear increase of the basal spacing is observed when the number of carbon atoms is increased from 10 to 18 (Fig. 9). As was established in previous work, the basal spacing \( d \) is related to the number of carbon in the alkyl chain \( n \) by the relation 
\[
\frac{d}{d_0} = 1.27 \cos(\theta)
\]
where \( \theta \) is the tilt angle of the chains with respect to the \( c \) axis. From this relation, it can be concluded that the alkyl chains are not parallel to the \( c \) axis but present a tilt angle close to 25–36° (Fig. 10), in very good agreement with previous findings for the Cu(II) parent compounds.32

Finally, it should be noted that the intercalation of nitrate or alkylsulfonate has no influence on the in-plane Ni–Ni distance that is equal to 2 \( d_{110} \). Indeed the corresponding reflection (20 ~ 60°) remains almost constant (\( d_{110} = 1.55 \) Å for all the compounds) and close to that of \( \beta \)-Ni(OH)\(_2\): 1.56 Å.

In conclusion, IR and X-ray diffraction studies show that the structural features of the obtained compounds depend mainly on the nature of the intercalated anion in two ways: (i) the length of this anion enables the layers to be spaced up to 32 Å apart, (ii) the head-group chemical functionality (sulfonate, nitrate, carboxylate) leads to several bond types with the nickel(II) ion. The magnetic properties are discussed hereafter in the light of these structural features.

### Table 2 Basal spacing and crystallite size

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basal spacing ( d/\text{Å} )</th>
<th>Crystallite size ( a/\text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHS-Ni-Ac</td>
<td>10.2</td>
<td>64</td>
</tr>
<tr>
<td>LHS-Ni-NO(_3)</td>
<td>7.5</td>
<td>65</td>
</tr>
<tr>
<td>LHS-Ni-C(_{10})SO(_3)</td>
<td>22.9</td>
<td>131</td>
</tr>
<tr>
<td>LHS-Ni-C(_{14})SO(_3)</td>
<td>25.9</td>
<td>185</td>
</tr>
<tr>
<td>LHS-Ni-C(_{18})SO(_3)</td>
<td>31.7</td>
<td>191</td>
</tr>
</tbody>
</table>

*Values inferred from the broadening of the first intense peak using Debye–Scherrer formula.

3.5. Magnetic properties

Magnetic measurements were performed in the temperature range 4–300 K, with an applied field \( H \approx 200 \) Oe. The temperature dependence of the inverse susceptibility \( \chi^{-1} \) and the \( \chi T \) product are plotted in Fig. 11 and 12. All the compounds exhibit the same magnetic behaviour. At high temperature, the observed values of the Curie constant \( C = N g^2 \mu_B^2 S(S + 1)/3k \), with \( S = 1 \) and the inferred \( g \) values are in good agreement with previous findings for octahedral nickel(II) (Table 3).

Upon cooling, both the variation of the \( \chi T \) product and the Curie–Weiss law with positive \( \theta \) value point to ferromagnetic in-plane interactions. The maximum of \( \chi T \), observed in the temperature range 16–18 K, may be related to the occurrence of 3D correlations. At lower temperature, a ferromagnetic state is well stabilized, as evidenced by the hysteric effect with increasing remanant magnetization and coercive field upon cooling. The plot of \( M \approx f(H) \) at \( T = 2 \) K for some compounds of the series is given in Fig. 13.

![Fig. 9 Basing spacing variation with the alkylsulfonate carbon number.](image)

![Fig. 8 Electron diffraction pattern of LHS-Ni-NO\(_3\).](image)

![Fig. 10 Idealized structural model for LHS-C\(_n\)H\(_{2n+1}\)SO\(_3\).](image)

![Fig. 11 Temperature dependence of (i) the inverse susceptibilities, (ii) the products of susceptibility and temperature of LHS-Ni-C\(_n\)H\(_{2n+1}\)SO\(_3\): (■) \( n = 10 \), (●) \( n = 14 \) and (∆) \( n = 18 \).](image)
Let us, now, compare the magnetic behaviour of the above compounds to that of \( \beta \)-Ni(OH)\(_2\), characterized by a basal spacing \( d \sim 4.6 \) Å. This hydroxide exhibits below 30 K a 3D AF order between ferromagnetic layers due to weak interplanar interactions via hydrogen bonds.\(^{33}\) In this compound, it has been established that the easy magnetization axis is perpendicular to the layers.\(^{34}\)

The same easy axis is observed for the title compounds. Indeed, magnetic measurements recorded for LHS-Ni-Ac pellets show low coercivity (370 Oe) when the applied field is perpendicular to the layers while it increases to 680 Oe for a field parallel to the pellet. Furthermore, the saturation magnetization is obtained at 2.7 T when \( H \) is normal to the layer while a significant canting is still present at 5 T in the perpendicular direction (Fig. 14).

Increasing the basal spacing weakens the interlayer hydrogen bonds, and accordingly the related interaction. Apparently, this one tends to vanish for an interlayer distance slightly less than 7.5 Å, as deduced from the magnetic behaviour of LHS-Ni-NO\(_3\). Such a character has been observed in nickel(II) phyllosilicates in which the Ni–Ni arrangement is similar to that of \( \beta \)-Ni(OH)\(_2\) and the basal spacing equal to 7 Å.\(^{35}\)

It should be pointed out that a distance of 7 Å appears to be a critical value. Indeed Rouba \textit{et al.}\(^{12}\) have reported a disordered ferromagnetic state for a nickel(II) hydroxynitrate showing as LHS-Ni-NO\(_3\) a brucite structure and an interlayer distance \( d \sim 6.9 \) Å. For more insight, we performed complementary ac susceptibility measurements which confirm the ferromagnetic character of the title nickel(II) hydroxynitrate. The in-phase (\( \chi' \)) and out-of-phase (\( \chi'' \)) components of the ac susceptibility confirm the ferromagnetic order at \( T \sim 20 \) K (Fig. 15) which is close to that deduced from dc measurements. Further, measurements performed at different frequencies (2 and 200 Hz) show that the critical temperature is frequency independent (Fig. 15) in agreement with ferromagnetic behaviour.\(^{36}\)

Drillon and Panissod\(^{37}\) have proposed a model to explain the magnetic behaviour of layered compounds in relation to their basal spacing. In this model, for in-plane ferromagnetic interactions, the in-plane spin moments align within correlation domains whose size increases upon cooling thus leading to giant magnetic moments for each layer. The interaction between these moments depends on the interlayer distance. For small distances, superexchange interaction occurs via hydrogen bonds and may lead to antiferromagnetic (or metamagnetic) order. In turn, for large distances, the through space dipole–dipole interaction between layers becomes predominant and favors long-range ferromagnetic order (for spins normal to the layers).

This model, successfully used to explain the magnetic behaviour of copper(II) and cobalt(II) parent compounds with magnetic layers up to 40 Å apart, shows that the variation of \( \beta \) (the unit cell parameters) has no significant effect on the critical temperature \( T_c \).

Let us, now, compare the magnetic behaviour of the above compounds to that of \( \beta \)-Ni(OH)\(_2\), characterized by a basal spacing \( d \sim 4.6 \) Å. This hydroxide exhibits below 30 K a 3D AF order between ferromagnetic layers due to weak interplanar interactions via hydrogen bonds.\(^{33}\) In this compound, it has been established that the easy magnetization axis is perpendicular to the layers.\(^{34}\)

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Table 3 Main magnetic results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basal spacing/Å</th>
<th>( T_c / K )</th>
<th>( \theta / K )</th>
<th>( H_c / Oe )</th>
<th>( M_s / m ) at 5 T</th>
<th>( g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHS-Ni-Ac</td>
<td>10.2</td>
<td>17</td>
<td>27</td>
<td>120</td>
<td>1.88</td>
<td>2.3</td>
</tr>
<tr>
<td>LHS-Ni-NO(_3)</td>
<td>7.5</td>
<td>16</td>
<td>18</td>
<td>1430</td>
<td>1.95</td>
<td>2.5</td>
</tr>
<tr>
<td>LHS-Ni-C(_6) SO(_3)</td>
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<td>11</td>
<td>240</td>
<td>1.36</td>
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<td>1990</td>
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</tr>
<tr>
<td>LHS-Ni-C(_{12}) SO(_3)</td>
<td>31.7</td>
<td>17</td>
<td>11</td>
<td>2310</td>
<td>1.72</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Fig. 12 Temperature dependence of (i) the inverse susceptibilities, (ii) the products of susceptibility and temperature of (O) LHS-Ni-NO\(_3\), (■) LHS-Ni-Ac.

Fig. 13 Isothermal magnetization at 2 K for (■) LHS-Ni-NO\(_3\), (○) LHS-Ni-C\(_n\)H\(_{2n+1}\)SO\(_3\) (\( n \sim 18 \)).

Fig. 14 Isothermal magnetization at 2 K on LHS-Ni-Ac oriented film. (O) Film perpendicular to the applied field, (■) film parallel to the applied field.

Fig. 15 Temperature dependence of the in-phase (\( \chi' \)) and out-of-phase (\( \chi'' \)) components of the ac susceptibility for LHS-Ni-NO\(_3\) at 2 (■) and 200 Hz (O).

J. Mater. Chem., 2002, 12, 3238–3244 3243
In the case of the nickel(n) compounds, it is worth noting that long-range ferromagnetic behaviour is observed whatever the interlayer distance in the range 7.5–32 Å. By varying the value of \( c/\alpha \) from 3 to 10 (the parameter \( \alpha \) was considered as almost constant and equal to 2 \( d_{\text{NiO}} \)) the variation of \( T_c \) is shown to be less than 2 K, in agreement with the model. The same critical temperature is observed for \( \text{Ni}_2(\text{OH})_2\text{C}_4\text{H}_4\text{SO}_3\cdot n\text{H}_2\text{O} \). Likewise, layered organic-inorganic nickel(n) silicates based on nickel(n) hydroxide sheets linked via organically modified silicate entities show close \( T_c \) values.\(^{38}\)

Thus, the critical temperature range 16–18 K appears to be a common feature of layered compounds based on nickel(n) hydroxide. Clearly, whether dipolar interactions between layers are needed to promote long range 3D order, the \( T_c \) value is mainly driven by the in-plane exchange interaction.\(^{37}\) This may appear questionable, upon considering the weak variation of the \( T_c \) value while the exchange interactions differ somewhat for the different exchanged compounds. In fact, there are two types of pathway, namely the hydroxyl groups and the exchanged anions which clearly have not the same weight in the overall exchange coupling. Thus, the intercalated anions, which substitute for some hydroxyl groups, present different bond types to the nickel(n) ions, as shown by IR studies, inducing significant change in the exchange pathways. However, as already emphasized in the cobalt(n) analogues, the leading interaction occurs through the \( \text{OH}^- \) bridging anions, so that the exchanged anion has a negligible influence on the overall interaction. It should however be noted that the Weiss constant (related to the short range interaction) appears to vary with the head-group chemical functionality of the intercalated anion. Acetate anion is located in the brucite sheets and bonded to the metal cations depending on the head-group functionality of the intercalated anion leading to the modification of the demagnetisation field when the basal spacing is increased.

### References