**On the Existence of Hydrotalcite-Like Phases in the Absence of Trivalent Cations**

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**INTRODUCTION**

The mineral hydrotalcite (HT) Mg₆Al₂(OH)₁₆CO₃·4H₂O together with other isotypic minerals, such as pyroaurite (1), reevesite (2), takovite (3), honesite (4), desaultesite (5), motukoreaitne (6), and iowite (7), belong to a general family of compounds known as layered double hydroxides (LDHs) (8). All the LDHs can be generally formulated as

$$M(OH)₂\text{·}x\text{H}^+ \rightarrow [M(OH)₂⁻\text{·}(H₂O)ₙ]^{x+}. $$

As in the LDHs, charge balance is restored by the incorporation of anions in the interlayer region. © 1997 Academic Press

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z-Hydroxides of nickel(II) and cobalt(II) are hydrotalcite-like phases, possessing a layered double hydroxide (LDH) structure even though there are no trivalent cations in the lattice. While the LDHs acquire a positive charge on the hydroxide layers by the incorporation of trivalent cations, we suggest that the z-hydroxides acquire a positive charge by partial protonation of the hydroxyl ions according to the equation

$$M(OH)₂\text{·}x\text{H}^+ \rightarrow [M(OH)₂⁻\text{·}(H₂O)ₙ]^{x+}. $$

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trivalent cations. In this paper, we present evidence toward this structural model and suggest that protonation of the hydroxyls is most likely the mechanism that incorporates a positive charge on $M(\text{OH})_2$ layers, leading to the formation of a HT-like structure for the $\alpha$-hydroxides.

**EXPERIMENTAL**

The $\alpha$-modification of nickel(II) hydroxide was synthesized electrochemically from aqueous solutions of various Ni salts such as nitrate, chloride, or sulfate. Platinum foils of 2 cm$^2$ area were used as electrodes. The hydroxide was deposited at the cathode from a 0.25 M salt solution galvanostatically at a current density of 25 mA cm$^{-2}$ for 10 h at room temperature (26–28°C). The product was separated from the electrode, filtered, washed with water, and dried at 100°C to constant weight. The $\alpha$-form of cobalt(II) hydroxide was synthesized similarly by cathodic reduction of a 0.1 M cobalt(II) nitrate solution containing 1 wt% of fructose as additive (17c). The solid products were characterized by powder X-ray diffractometry (XRD) (JEOL JDX-8P powder diffractometer), infrared spectroscopy (Perkin–Elmer 580 Infrared spectrometer, KBr pellets), and thermogravimetric (TG) analysis. The solid products were also characterized by wet chemical analyses. The metal contents of the hydroxides were estimated gravimetrically using standard methods. The hydroxyl contents were determined by dissolving a known quantity of the solid in excess of 0.4 M HCl, and then back-titrating the excess acid with standard NaOH using a pH meter. The chloride and sulfate contents, where applicable, were estimated gravimetrically by precipitation as AgCl and BaSO$_4$, respectively. The unaccounted weight was attributed to the water content. On the basis of the analytical results, we give the compositions of the $\alpha$-hydroxides of nickel(II) containing nitrate, chloride, and sulfate ions in Table 1. The total weight losses found from TG analyses are in agreement with the compositions (see Table 1).

**TABLE 1**

<table>
<thead>
<tr>
<th>Ni(OH)$_2$ obtained from</th>
<th>Composition (wt%)$^a$</th>
<th>% Wt. loss$^b$ (TG)</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NO$_3$)$_2$</td>
<td>Ni 51.2, OH$^-$ 26.9, A$^-$ 11.2, H$_2$O 10.7</td>
<td>35.6 (34.1) Ni(OH)$_{1.4}$(NO$<em>3$)$</em>{0.2}$(H$<em>2$O)$</em>{0.65}$</td>
<td></td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>Ni 51.5, OH$^-$ 26.2, A$^-$ 6.8, H$_2$O 15.5</td>
<td>34.0 (34.5) Ni(OH)$<em>{1.6}$(Cl)$</em>{0.5}$(H$<em>2$O)$</em>{0.98}$</td>
<td></td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>Ni 50.9, OH$^-$ 24.5, A$^-$ 12.4, H$_2$O 12.3</td>
<td>25.4 (25.4) Ni(OH)$_{1.6}$(SO$<em>4$)$</em>{0.1}$(H$<em>2$O)$</em>{0.79}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All compositions are reported within an error of 1%.

$^b$ Values in parentheses correspond to the expected weight loss as calculated from the molecular formula. The product of decomposition is NiO for nitrate and chloride containing hydroxides and NiO + NiSO$_4$ for the sulfate containing hydroxide.
The absence of trivalent cations in \(\alpha\)-hydroxides was checked by reactions with excess ferrous ammonium sulfate and back-titrating the excess with standard potassium dichromate. Comparison with a blank titration confirmed the absence of any trivalent ions in the \(\alpha\)-hydroxides.

**RESULTS AND DISCUSSION**

Chemical analysis of the \(\alpha\)-nickel hydroxides obtained from the nitrate, chloride, and sulfate solutions (Table 1) shows that the compositions can be expressed by the general formula \([\text{Ni(OH)}_{\alpha}x_{x-\alpha}\text{(H}_2\text{O)}]^{\alpha+}A_{\alpha}^{\alpha-}\) revealing the presence of a definite amount of anions and water molecules besides the hydroxyl ions. Investigations of \(\alpha\)-cobalt hydroxides also yielded similar results.

We show in Fig. 2 the powder XRD patterns of \(\alpha\)-nickel hydroxide and a laboratory synthesized nitrate analog of takovite having the formula \(\text{Ni}_{0.75}\text{Al}_{0.25}(\text{OH})_{2\alpha}\text{(NO}_3\text{)}_{0.25}\cdot0.5\text{H}_2\text{O}\). We also show the XRD patterns of \(\alpha\)-cobalt hydroxide and the Co–Al LDH \((\alpha = 0.25)\). In Table 2 we list the \(d\) values for the prominent \(hkl\) reflections of the \(\alpha\)-hydroxides and compare them with those of the Ni–Al and Co–Al LDHs. It is at once evident that the \(\alpha\)-hydroxides are isostructural with the LDH phases.

In Fig. 3 we show the infrared spectra of a typical \(\alpha\)-hydroxide and compare it with that of a LDH. In both spectra, strong vibrations due to intercalated anions (1470, 1380, 1310, 1050, 1000 cm\(^{-1}\) for nitrate) are seen in the 1400–900 cm\(^{-1}\) region. The sulfate containing hydroxides show strong vibrations at 1124 and 1047 cm\(^{-1}\) while the chloride containing hydroxides do not show any absorption in this region as expected. Further, the OH stretch in the LDHs as well as the \(\alpha\)-hydroxides appears as a broad band centered around 3450 cm\(^{-1}\), revealing that the hydroxyls are involved in hydrogen bonding with the intercalated water molecules. These spectral features of the \(\alpha\)-hydroxides are consistent with the chemical compositions given in Table 1. On the other hand brucite-like \(\beta\) hydroxides show a strong sharp OH stretch around 3650 cm\(^{-1}\) which indicates the presence of nonhydrogen bonded OH groups.

These results show that, in terms of both long range and short range structure, the \(\alpha\)-hydroxides of nickel and cobalt are HT-like phases, containing a definite amount of intercalated anions, even though there are no trivalent cations. While the relationship between the LDH and \(\alpha\)-hydroxides has not been established.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>(\alpha)-Nickel hydroxide</th>
<th>Ni–Al LDH</th>
<th>(\alpha)-Cobalt hydroxide</th>
<th>Co–Al LDH</th>
</tr>
</thead>
<tbody>
<tr>
<td>003</td>
<td>7.560</td>
<td>7.890</td>
<td>7.915</td>
<td>7.550</td>
</tr>
<tr>
<td>006</td>
<td>3.780</td>
<td>3.895</td>
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<tr>
<td>101</td>
<td>2.670</td>
<td>2.540</td>
<td>2.627</td>
<td>2.586</td>
</tr>
<tr>
<td>105</td>
<td>2.340</td>
<td>2.317</td>
<td>2.322</td>
<td>2.309</td>
</tr>
<tr>
<td>107</td>
<td>2.030</td>
<td>2.222</td>
<td>2.112</td>
<td>1.938</td>
</tr>
<tr>
<td>110</td>
<td>1.550</td>
<td>1.499</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(d_{\text{observed}}/\AA\)

\(a = 3.10\,\AA\) \(c = 22.68\,\AA\) \(a = 3.09\,\AA\) \(a = 3.09\,\AA\) \(a = 3.09\,\AA\) \(c = 22.65\,\AA\)

FIG. 2. Power X-ray diffraction patterns of \(\alpha\)-nickel(II) hydroxide (a), nitrate intercalated synthetic takovite (b), \(\alpha\)-cobalt(II) hydroxide (c), and Co–Al LDH (d). The patterns at (c) and (d) have been recorded with CoK\(\alpha\) \((\lambda = 1.790\,\AA)\) radiation. The feature marked with an asterisk is an impurity peak due to \(\beta\)-cobalt hydroxide.

FIG. 3. Infrared spectra of \(\alpha\)-nickel(II) hydroxide (lower curve) compared with that of nitrate intercalated synthetic takovite (upper curve).
to LDHs, except that the same metal exists in the (II) and (III) states in the \( \text{x-hydroxide} \).

(b) Faure et al. (19) and Delahaye-Vidal et al. (20) suggested the presence of hydroxyl vacancies in the \( \text{x-hydroxide} \) layers, leading to the incorporation of anions in the interlayer space for charge balance.

(c) Bish and Livingstone (21) proposed inclusion of cation–anion pairs in the interlayer region. Such cation–anion pairs have indeed been found in the mineral hydrohonesite.

(d) A fourth possibility is the direct coordination of the anions to the metal, as in hydroxysalts (22) such as \( \text{Ni(OH)}_2 (\text{NO}_3)_2 \).

(e) A fifth possibility involves incorporation of additional \( \text{M(II)} \) cations at interstitial (tetrahedral) sites of the \( \text{x-hydroxide} \) layers (23). This possibility is realized in the layered hydroxynitrate, \( \text{Zn}_4 (\text{OH})_8 (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \), where one-fourth of the \( \text{Zn(II)} \) at octahedral sites is replaced by pairs of tetrahedrally coordinated \( \text{Zn(II)} \) on each side of the hydroxylayer giving the layer composition, \( [\text{Zn}_4 (\text{OH})_8]^{2+} \). This compound crystallizes in a monoclinic structure \((a = 19.48 \, \text{Å}, b = 6.238 \, \text{Å}, c = 5.517 \, \text{Å}, \text{and} \beta = 93.28) \) and is not isostructural with either the LDHs or the \( \text{x-hydroxides} \) despite having a composition similar to the latter, \( \text{Zn(OH)}_2 \cdot _x (\text{NO}_3)_2 \cdot m\text{H}_2\text{O} \) \((x = 0.4; m = 0.4) \).

All the above models for \( \text{x-hydroxides} \) can be discounted on the basis of experimental data except probably model (b). Model (a) is inappropriate because there is no detectable \( \text{Ni(III)/Co(III)} \) in the \( \text{x-hydroxides} \); the hydroxides are green/green-blue in color. Model (b), suggesting that hydroxyl vacancies in \( \text{M(OH)}_2 \) layers are occupied by anions, does not bring out the actual mechanism of incorporation of positive charge on the hydroxide layers. Model (c) could be ruled out because inclusion of cation–anion pairs would result in much larger interlayer spacings \((\sim 11 \, \text{Å}) \). Such large interlayer spacings are not seen for the \( \text{x-hydroxides} \). Model (d) also could be ruled out considering that this model should lead to much smaller interlayer spacing \((\sim 6.9 \, \text{Å}) \) than what is observed for the \( \text{x-hydroxides} \). Model (e) is obviously inappropriate for the \( \text{x-hydroxides} \) because nickel(II) normally does not occupy tetrahedral sites in oxides/hydroxides. Even cobalt(II) does not go to tetrahedral sites when the synthesis is carried out in aqueous media. Moreover, a tetrahedral cobalt(II) would have imparted a distinct blue color to the sample and led to a monoclinic structure as in the case of zinc hydroxynitrate.

A most likely model for the \( \text{x-hydroxides} \), which would account for the inclusion of anions as well as water molecules in the interlayer space, would be partial protonation of the hydroxyls giving rise to a net positive charge on the \( \text{x-hydroxide} \) layers,

\[
\text{M(OH)}_2 + x\text{H}^+ \leftrightarrow [\text{M(OH)}_{2-x}(\text{H}_2\text{O})_x]^x^+.
\]

The extent of protonation and hence the magnitude of the positive charge on the hydroxide layers would depend on the hydrolysis behavior of \( \text{M(II)} \) ions in aqueous media (24). This model would also account for the surprisingly high proton diffusion coefficient of \( \text{ nickel(II) hydroxide} \) (25) which enables the \( \text{x-hydroxides} \) to function as electrode materials in alkaline secondary batteries.

**SUMMARY**

In conclusion, we suggest that a partial protonation of the hydroxyls of the \( \text{M(OH)}_2 \) layers is the most likely mechanism for the incorporation of positive charge on the layers that gives rise to anion and water intercalated \( \text{x-hydroxides} \) of these metals.

**ACKNOWLEDGMENT**

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**REFERENCES**