Chem. Mater. **1999,** *11,* 303−307

Layered Double Hydroxide Stability. 2. Formation of Cr(III)-Containing Layered Double Hydroxides Directly from Solution

Joseph W. Boclair, Paul S. Braterman,* Jianping Jiang, Shaowei Lou, and Faith Yarberry

Departments of Chemistry and Materials Characterization, University of North Texas, Denton, Texas 76203-5070

Received July 23, 1998. Revised Manuscript Received November 23, 1998

Solutions containing divalent metal [M(II) = Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}] chlorides and $CrCl_3{\cdot}6H_2O$ were titrated with NaOH to yield, for M(II) = Zn, Co, and Ni, hydrotalcite-like layered double hydroxides (LDHs), $[[M(II)]_{1-z}[Cr(III)]_z(OH)_2][Cl]_z{\cdot}yH_2O$, in a single step, without intermediate formation of chromium hydroxide. Analysis of the resultant titration curves yields solubility constants for these compounds. These are in the order Zn < Ni ≈ Co, with a clear preference for formation of the phase with $z = {}^1/_3$. With Mg^{2+} as chloride, titration gives a mixture of $Cr(OH)_3$ and $Mg(OH)_2$, but the metal sulfates give $Mg_2Cr(OH)_6{\cdot}{}^1/_2(SO_4)$ by a two-step process. Titrimetric and spectroscopic evidence suggests short-range cation order in the one-step LDH systems.

Introduction

The importance of layered double hydroxides (LDHs) is discussed and documented in the preceding paper.[1] Some aspects of our work with the Zn(II):Cr(III) LDH system have been described in a preliminary communication.[2] Known LDHs in which the trivalent metal is chromium include $Zn_2Cr(OH)_6X$,[3−5] $Ni_2Cr(OH)_6X$,[5−7] $Cu_2Cr(OH)_6X$,[8] and the mineral barbertonite, ($Mg_2Cr(OH)_6(CO_3)_{1/2}$).[9] Zinc−chromium(III) LDHs are particularly easy to prepare, forming when solid ZnO is exposed to a solution of chromium(III) chloride.[3]

Layered double hydroxides are commonly prepared by addition of base to solutions containing a mixture of M(III) and M(II).[5,10−12] When M(III) = Fe or Al, M(III) hydr(ous) oxides are initially formed. Further addition of base results in conversion of the M(III) hydr(ous) oxide to LDH, and we have shown that monitoring the solution pH throughout this process provides enough information to calculate quantitative solubility data for the precipitated LDH.[1] The more soluble the M(III) hydr(ous) oxide, the higher the pH of the first plateau and the lower the pH of the second. The pH of the second plateau was also lower for the more *in*soluble $M(II)(OH)_2$. We inferred that for a sufficiently *soluble* M(III) hydr(ous) oxide, and a sufficiently *insoluble* M(II) hydroxide, the pH of the "second" plateau might well fall below that of the "first." This would correspond to direct formation of LDH from solution, without the intermediacy of a precursor solid phase. Such a situation would hold out improved prospects for the formation of LDH with controlled morphologies or as films. We now report that those expectations are realized when M(III) = Cr and M(II) = a late transition metal, and we adapt our earlier quantitative treatment to this situation.

Experimental Section

Materials and methods used are as described previously.[1] Additionally, for this work, we used $CrCl_3{\cdot}6H_2O$ and $Cr_2(SO_4)_3{\cdot}xH_2O$ as supplied by Aldrich and $MgSO_4{\cdot}7H_2O$ as supplied by Spectrum Chemical Manufacturing.

To better study the nature of the preferred LDH phase in these one-step processes, solutions were prepared 0.1 M in Cr(III) and 0.1, 0.2, or 0.3 M in M(II) chloride (M(II) = Zn, Co, Ni). In all cases, sodium chloride was added to maintain an overall chloride concentration of 1.0 M. All the 3:1 and 1:1 M(II):Cr(III) solutions were also separately titrated to approximately 92% of the end point required for formation of the 2:1 LDH and the resulting solids collected for characterization. Solutions containing Zn(II):Cr(III) ratios of 1:1 and 3:1 were also prepared and titrated to 92% of the end point corresponding to the solution metal ratio. These solids, nominally $ZnCr(OH)_4Cl$ and $Zn_3Cr(OH)_8Cl$, were then collected for analysis.

Solutions of the individual metal chlorides had been previously titrated in the absence of other metal ions.[1] In this work, chromium(III) chloride was also titrated in the absence of other metals for purposes of comparison.

Infrared spectra and powder X-ray diffraction data were collected as described previously.[1] Ultraviolet−visible diffuse

---

* To whom correspondence should be addressed. E-mail: psb@unt.edu.

(1) Boclair, J. W.; Braterman, P. S. *Chem. Mater.* **1999**, *11*, 298 (preceding paper in this issue).

(2) Boclair, J. W.; Braterman, P. S. *Chem. Mater.* **1998**, *10*, 2050.

(3) Boehm, H.-P.; Steinle, J.; Vieweger, C. *Angew. Chem., Int. Ed. Engl.* **1977**, *4*, 265.

(4) Ennadi, A.; Khaldi, M.; De Roy, A.; Besse, J.-P. *Mol. Cryst. Liq. Cryst.* **1994**, *244*, 373.

(5) de Roy, A.; Forano, C.; El Malki, K.; Besse, J.-P. In *Synthesis of Microporous Materials*; Occelli, M. L., Robson, H. E., Eds.; Van Nostrand Reinhold: New York, 1992; Vol. 2, p 108.

(6) Clause, O.; Gazzano, M.; Trifiró, F.; Vaccari, A.; Zatorski, L. *Appl. Catal.* **1991**, *73*, 217.

(7) Kooli, F.; Rives, V.; Ulibarri, M. A. *Inorg. Chem.* **1995**, *34*, 5122.

(8) Depege, C.; Bigey, L.; Forano, C.; de Roy, A.; Besse, J. P. *J. Solid State Chem.* **1996**, *126*, 314.

(9) Taylor, H. F. W. *Miner. Magn.* **1973**, *39*, 377.

(10) Feitknecht, W.; Gerber, M. *Helv. Chim. Acta* **1942**, *25*, 131.

(11) Feitknecht, W. *Helv. Chim. Acta* **1942**, *25*, 555.

(12) Treadwell, W. D.; Bernasconi, E. *Helv. Chim. Acta* **1930**, *13*, 500.

10.1021/cm980524m CCC: $18.00

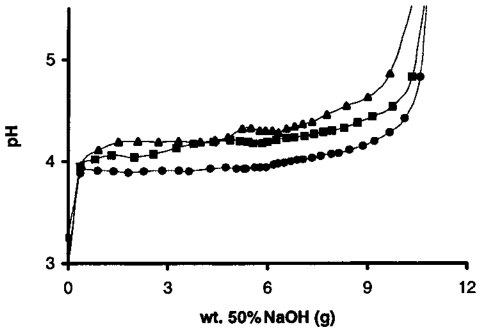

Figure 1. Titration curves of 2:1 $ZnCl_2$:$CrCl_3$ (●), $CoCl_2$:$CrCl_3$ (■), and $NiCl_2$:$CrCl_3$ (▲) solutions.

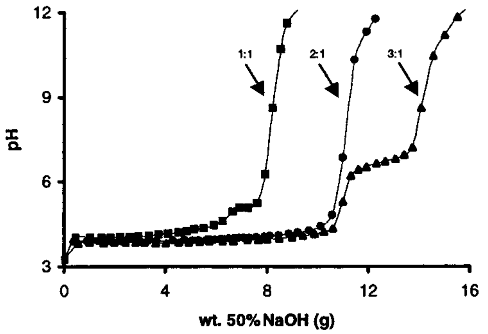

Figure 2. Titration curves of 1:1 (■), 2:1 (●), and 3:1 (▲) Zn(II):Cr(III) solutions.

reflectance spectra were collected on a Perkin-Elmer Lambda 9 spectrometer equipped with a 60 mm integrating sphere attachment. Elemental analysis for metal content was performed using a Perkin-Elmer 5500 ICP, for which all samples were dissolved in a 5% HNO_3 solution prior to analysis. Standard metal solutions from Aldrich and Alfa Æsar were used as calibrants for all ICP measurements.

Results and Discussion

As discussed earlier,[1] a typical titration curve for mixed-metal solutions containing Al^{3+} or Fe^{3+} shows two distinct buffer regions or plateaus, corresponding to formation of the trivalent metal hydroxide or hydrous oxide and the formation of the layered double hydroxide, respectively.[12,13] The higher the solubility of the trivalent hydr(ous) oxide, the higher the pH of the first plateau and, for a given divalent metal, the lower the pH of the second plateau. Hence, our prediction (see Introduction) that, for a sufficiently soluble $M(III)(OH)_3$ and a sufficiently insoluble $M(II)(OH)_2$, the LDH will be formed directly from solution, without the intermediacy of $M(III)(OH)_3$. We now report that this prediction is fulfilled in the cases involving Cr^{3+} with Zn^{2+}, Co^{2+}, or Ni^{2+}. Here the transition is completely absent and the LDH is formed in preference to $M(III)(OH)_3$ from the start of the titration. The pH of the LDH formation plateau in all these cases is lower than that for the formation of $Cr(OH)_3$ when Cr(III) is titrated on its own and, as expected, is dependent on the identity of the divalent metal used.

Figure 1 shows the titration curves for 2:1 solutions of Zn(II):Cr(III), Co(II):Cr(III), and Ni(II):Cr(III). In contrast to the two-step processes described in the accompanying paper,[1] these curves demonstrate one-step LDH formation, as shown by the single buffer region with end point corresponding to a Cr(III):(OH^-) ratio of 1:6, and no evidence for the formation of $Cr(OH)_3$. Moreover, sampling of the solid at various times during a given titration for infrared analysis shows that the same material is formed throughout. We infer that the precipitation of LDH is taking place directly from solution without the formation of a precursor M(III) hydroxide phase, in contrast to the related systems in which M(III) = Al or Fe.

This one-step formation of the $x = 2$ LDH removes the necessity to consider the solubility of the Cr(III) hydr(ous) oxide. One can derive nominal solubility product constants directly from the pH of the LDH plateau region. Once calculated, these data may be used to quantify the relative stabilities of layered double hydroxide systems.

Table 1. Inferred pK_{sp} for Formation of $[M(II)]_2Cr(OH)_6Cl$ from Solutions of Varying M(II):Cr Content

M(II):M(III)	1:1	2:1	3:1
Co:Cr	62.53	62.11	62.07
Ni:Cr	61.88	61.83	61.62
Zn:Cr	63.18	63.57	63.23

The titration curves of Zn(II):Cr(III) solutions having Zn(II):Cr(III) ratios of 1, 2, and 3 are compared in Figure 2. Titration of solutions containing M(II):Cr(III) ratios other than 2 (M(II) = Zn, Co, Ni) showed a preference for the formation of the 2:1 LDH. For M(II):Cr 3:1, the titration curve showed two regions. The first of these was identical to that observed for the 2:1 case, with a transition point corresponding quantitatively to the formation of material with $x = 2$, while the second was in the correct position for the precipitation of $M(II)(OH)_2$. These results mirror those reported by de Roy and El Malki for the 3:1 Zn(II):Cr(III) and Ni:Cr systems.[5] Similarly, when the M(II):Cr ratio was 1:1, we found two regions, of which the first corresponds to formation of the material with $x = 2$, while the second was at the correct pH for formation of $Cr(OH)_3$.

For the reasons discussed above, in the observed one-step titrations and the first plateau of solutions with M(II):Cr(III) ≠ 2, we consider that the 2:1 LDH product is the first material to be formed from solution. The concentration of $M(II)^{2+}$ and Cr^{3+} remaining in solution can be adequately estimated by assuming stoichiometric precipitation of the metals by hydroxide. Given the difficulties in assigning activity coefficients at the high ionic concentrations used, we again make no attempt to correct for these. For the purposes of calculation, we assume the simple, direct formation of the appropriate 2:1 layered double hydroxide. Taking these assumptions into consideration, a nominal K_{sp} for the overall formation of a layered double hydroxide from the metal ions, hydroxide, and chloride

$$Cr(III)M(II)_2(OH)_6Cl \rightleftharpoons Cr^{3+} + 2M(II)^{2+} + 6OH^- + Cl^- \quad (1)$$

may be inferred from the expression

$$K_{sp,LDH} = [Cr^{3+}][M(II)^{2+}]^2[OH^-]^6[Cl^-] \quad (2)$$

The results of these calculations are shown in Table 1. Different M(II):Cr(III) ratios yield similar inferred K_{sp} values for the 2:1 LDH, strongly supporting our claim

---

(13) Turner, R. C.; Brydon, J. E. *Science* **1962**, *136*, 1052.

Table 2. Elemental Analysis Data for Zn(II):Cr(III) LDH Chlorides Obtained from Solutions of Varying Zn(II):Cr(III) Ratio

soln Zn:Cr	% Zn(II)	% Cr(III)	solid Zn:Cr
3:1	33.35	13.11	2.02
2:1	30.57	12.51	1.94
1:1	29.02	13.30	1.74

Table 3. Inferred Equilibrium Constants for $[M(II)]_2Cr(OH)_6Cl$ (K_{sp} Values for Metal Hydroxides from This Work[a])

	Co	Ni	Zn
log $K_{form,LDH}$	33.54	33.25	35.05
log $K_{conv,LDH}$	5.18	5.17	2.35

[a] For $Cr(OH)_3$, we find pK_{sp} = 28.36. K_{sp}'s for $M(OH)_2$ from Reference 1.

Table 4. Observed Infrared Frequencies for 2:1 M(II):Cr(III) LDHs

M(II)	anion	ν(OH)	δ(OH)	$\nu,\delta(SO_4{}^{2-})$	lattice vibrations
Co	Cl^-	3392	1620		710, 561, 506
	$SO_4{}^{2-}$	3398	1626	1107, 618	719, 564, 505
Ni	Cl^-	3403	1621		680, 566, 517, 405
	$SO_4{}^{2-}$	3398	1632	1109, 619	707, 656, 520, 405
Zn	Cl^-	3392	1620		706, 567, 508
	$SO_4{}^{2-}$	3381	1642	1107	706, 570, 509

Table 5. Basal Spacings for 2:1 Cr(III)-Containing LDHs in Å (This Work from [006])

	chloride	sulfate
Co:Cr	7.78	10.83
Ni:Cr	7.69 (7.74[a])	8.94 (8.75[a])
Zn:Cr	7.80 (7.75[b])	10.70 (11.07[b])

[a] From ref 5. [b] From ref 15.

that the nominal 2:1 phase is the one first formed in all these cases. Additionally, ICP analysis of solids obtained in these various titrations showed that the M(II):Cr(III) ratios in the favored product were fairly insensitive to those present in solution, with the Zn(II):Cr(III) ratios ranging from 1.74 for the 1:1 Zn(II):Cr(III) solution to 2.02 for the 3:1 solution. Zn:Cr ratios in these solids and inferred nominal compositions (assuming two OH^- for each metal ion and one Cl^- for each Cr) are shown in Table 2.

For a given two-step titration, the constant of the formation of LDH from an existing "M(III)(OH)$_3$" phase, a process illustrated by eq 3, is defined by eq 4.

$$\text{“}M(III)(OH)_3\text{”} + 2M(II)^{2+}{}_{(aq)} + 3OH^- + Cl^- \rightleftharpoons M(III)[M(II)]_2(OH)_6Cl \quad (3)$$

$$K_{form,LDH} = \{[M(II)^{2+}]^2[OH^-]^3[Cl^-]\}^{-1} \quad (4)$$

This equation however is only valid if the solution is saturated with $M(III)(OH)_3$. Despite the lack of a solid $M(III)(OH)_3$ phase in the present case, one can calculate the notional ease of formation of the LDH from the trivalent metal hydroxide using eq 5:

$$K_{form,LDH} = K_{sp,}M(III)(OH)_3/K_{sp,LDH} \quad (5)$$

Finally, we note that the equilibrium constant for the reaction

$$M(III)(OH)_3 + 2M(II)(OH)_2 + Cl^- \rightleftharpoons [M(II)]_2M(III)(OH)_6Cl + OH^- \quad (6)$$

in which a mixture of simple hydroxides is converted to LDH is given, as before, by

$$\log K_{conv,LDH} = \log K_{form,LDH} + 2 \log K_{sp,M(II)(OH)_2} \quad (7)$$

Table 3 summarizes the log $K_{form,LDH}$ and log $K_{conv,LDH}$ values for the Zn, Ni, and Co systems. These values follow the same trends shown previously for Al- and Fe-containing LDHs.[1] As discussed previously,[1] we utilize our own data for $K_{sp,M(OH)_2}$ in calculating $K_{conv,LDH}$, so that $K_{conv,LDH}$ is expressed relative to the immature metal hydroxides (and LDH) under uniform experimental conditions. The positive values of log $K_{conv,LDH}$ seen for these systems indicate that the LDH chloride is predicted to be thermodynamically more stable than a mixture of the separate hydroxides, even in the presence of equal amounts of hydroxide and chloride. Of the systems discussed earlier,[1] this was only the case with the Mg:Al system.

Infrared analysis of the products from the 2:1 solutions show spectra indicative of a well-ordered double layer material (Table 4). Particularly significant are the sharp bands near 510 cm^{-1}, reminiscent of annealed (but not freshly precipitated) $Mg_2Al(OH)_6Cl$.[14] Diffuse reflectance UV–vis spectra show, as expected, octahedrally coordinated Cr(III) ions, the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ occurring at 17 800 and 24 960 cm^{-1} respectively for the 2:1 Zn(II):Cr(III) LDH chloride. The $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transition cannot be observed, as it is masked by a LMCT band. In addition, the materials were examined by powder XRD and show the expected diffraction patterns of layered materials with basal spacings from 7.69 Å for Ni(II):Cr(III) to 7.80 Å for Zn(II):Cr(III). Finally, the materials were exposed to 0.1 M solutions of sodium sulfate for 24 h, to replace chloride with sulfate. As expected, the exchanged materials showed new infrared bands at 1188, 1109, and 615 cm^{-1}, due to sulfate, and expansion of the interlayer spacing to either 8.8 or 11.00 Å (Table 5). This variability in gallery height of sulfate-containing materials has also been observed by other workers and attributed to changes in the hydration of the LDH.[16]

As stated previously, the initial product formed in any of the titrations involving Cr(III) and Zn(II), Co(II), or Ni(II) was a nominally 2:1 LDH system. Products formed after the 2:1 end point in either the 1:1 or 3:1 cases are not so easily identified. The titration data suggest that, following the formation of the 2:1 LDH, the excess metal is then precipitated as the hydroxide or hydr(ous) oxide, on top of the LDH, creating a mixed solid phase. However, the titration curves, by themselves, cannot distinguish between the formation, in the second stage of precipitation, of a mixture of the $x = 2$ material and the hydroxide of the metal present in excess and the formation at similar free energies of phases with x higher or lower than the preferred value. Elemental analysis results for materials prepared to be nominally 1:1, 2:1, and 3:1 M(II):Cr(III) LDHs are listed in Table 6, but such results, of their nature, could not

---

(14) Boclair, J. W.; Braterman, P. S.; Jiang, J.; Lou, S.; Yarberry, F. In press.

(15) El Malki, K.; Guonano, M.; Forano, C.; de Roy, A.; Besse, J. P. *Mater. Sci. Forum* **1992**, *91–93*, 171.

(16) Bookin, A. S.; Drits, V. A. *Clays Clay Miner.* **1993**, *41*, 551.

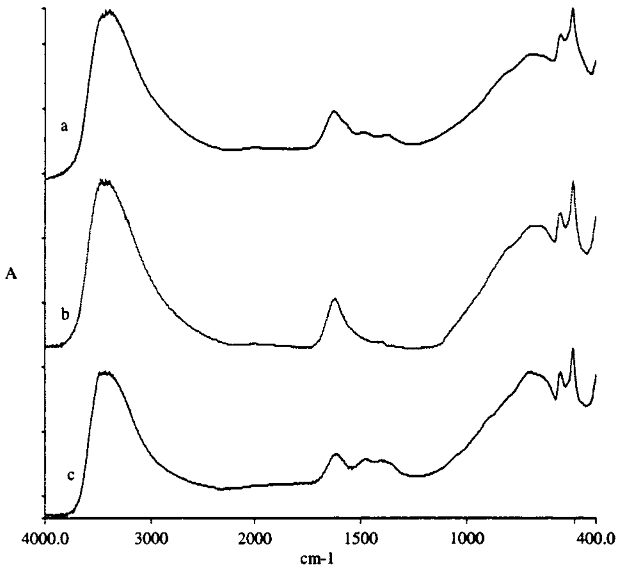

Figure 3. FTIR spectra of 1:1 (a), 2:1 (b), and 3:1 (c) Zn(II):Cr(III) LDH Cls.

Table 6. Elemental Analysis Data for 1:1, 2:1, and 3:1 M(II):Cr(III) LDHs

			M:Cr	
M(II)	% M(II)	% Cr(III)	theor	obsd
Co	24.02	20.81	1	1.02
	33.38	14.36	2	2.01
	31.26	9.97	3	2.77
Ni	20.06	17.67	1	1.00
	23.99	10.79	2	1.97
	26.14	7.87	3	2.94
Zn	24.97	19.39	1	1.03
	26.75	10.80	2	1.97
	28.65	7.23	3	3.15

be used to distinguish a single phase from a mixture of 2:1 LDH and excess metal hydroxide.

Infrared and powder XRD analysis are also little help in distinguishing between, for instance, 3:1 LDH and a mixture of 2:1 LDH and M(II)$(OH)_2$. Figures 3 and 4 present the infrared and powder XRD patterns of 1:1, 2:1, and 3:1 Zn(II):Cr(III) LDHs. The infrared spectrum (Figure 3) in the regions 3600−3000 cm^{-1} and 600−400 cm^{-1} is dependent on the identity of M(II) but independent of the M(II):Cr ratio in the solid. By contrast, in the Mg(II):Al(III), Ni(II):Al(III),[17] and Co(II):Al(III)[18] systems, where 2:1 and 3:1 materials are both well-characterized, there are clear differences between them in these regions. Powder XRD data show little, if any, variation between LDHs of varying Zn(II):Cr(III) ratios, but this does not exclude the possible formation of "amorphous" Cr(III) or Zn(II) hydroxide. However, diffuse reflectance UV−vis spectra obtained for Zn(II):Cr(III) materials with varying Zn(II):Cr(III) ratios show a dependence of the ligand field of Cr(III) on the Zn(II):Cr(III) ratio. Table 7 summarizes these results. Our research shows that the ligand field at Cr(III), based on diffuse reflectance UV−vis data, varies from 17 310 cm^{-1} for a 1:1 material, through 17 800 cm^{-1} for the 2:1 material (see above), to 18 040 cm^{-1} for a 3:1 material.

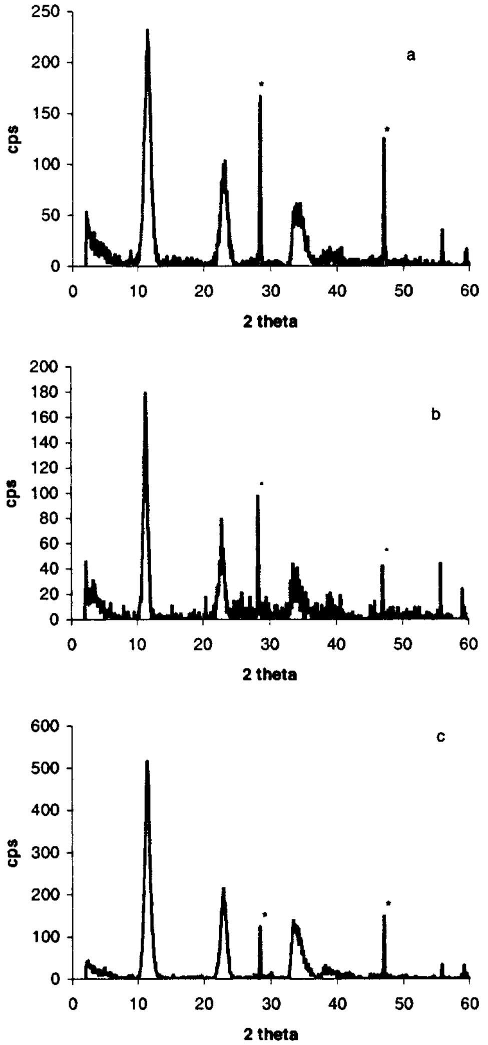

Figure 4. Powder XRD traces of 1:1(a), 2:1 (b), and 3:1 (c) Zn(II):Cr(III) LDH Cls (* indicates reference peak).

Table 7. Diffuse Reflectance UV−Vis Absorption Maxima (cm^{-1}) for Zn:Cr LDHs

compound	Zn:Cr	$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{1g}(F)$	ref
$[Cr(H_2O)_6]^{3+}$		17 400	24 700	22
"$Cr(OH)_3$"		17 010	23 660	*a*
$ZnCr(OH)_4Cl$	1.03	17 310	24 180	*a*
$Zn_7Cr_4(OH)_{22}(CO_3)_2$	1.75	17 480	24 500	20
$Zn_2Cr(OH)_6Cl$	1.97	17 800	24 960	*a*
$Zn_2Cr(OH)_6(CO_3)_{0.5}$	2.00	17 900	25 570	20
$Zn_3Cr(OH)_8Cl$	3.15	18 040	24 860	*a*

[a] This work.

This does not seem consistent with the formulation of the 1:1 and 3:1 materials as mixtures. Gutmann and Müller have recently inserted the $[Cr(\mu\text{-}OH)_2Cr]^{4+}$ unit into Zn(II):Cr(III) LDHs.[19] The existence of this dimer in Zn(II):Cr(III) LDHs is consistent with the ease with which these "one-step" LDHs form with M(II):Cr ratios less than 2; in direct contrast to the observed trends for Al- and Fe-containing LDHs.[20]

One of the most important questions concerning LDHs is the issue of cation order. Long-range cation order has been established in very few LDH systems, mainly Mg(II):Ga(III),[21] Al(III):Li(I)-containing LDHs,[22,23]

---

(17) Hernandez-Moreno, M. J.; Ulibarri, M. A.; Rendon, J. L.; Serna, C. J. *Phys. Chem. Miner.* **1985**, *12*, 34.

(18) Kannan, S.; Velu, S.; Ramkumar, V.; Swamy, C. S. *J Mater. Sci.* **1995**, *30*, 1462.

(19) Gutmann, N.; Müller, B. *J. Solid State Chem.* **1996**, *122*, 214.

(20) Miyata, S. *Clays Clay Miner.* **1980**, *28*, 50.

and some Mg(II):Fe(III) mineral specimens.[24] Short-range cation order, in the absence of long-range order, has also been demonstrated for synthetic Mg(II):Fe(III) LDHs.[25] While the evidence here is indirect, we feel that it is very suggestive of short-range cation order in the Zn(II):Cr(III) LDH chloride for the following reasons.

(1) Titration of solutions having Zn(II):Cr(III) ratios ranging from 1:1 to 3:1 all show preference for initial formation of a phase having $x = 2$. This corresponds to an ideal ratio of ordered cations in the hydroxyl layer. We have further confirmed this ratio by elemental analysis (ICP) of the product.

(2) The infrared spectrum in the region between 600 and 400 cm^{-1} is dependent on the identity of M(II) but is independent of the M(II):Cr ratio in the precursor solution. By contrast, in the Mg(II):Al(III) system, where 2:1 and 3:1 materials are both well-characterized, there are clear differences between them in this region.[17]

(3) The 447 cm^{-1} band, characteristic of 2:1 Mg(II):Al(III) LDH is absent in freshly precipitated material but develops on refluxing overnight.[14] For the materials discussed here, the sharp peak at about 510 cm^{-1} is present from the outset.

(4) The electronic diffuse reflection spectrum shows absorption maxima at 17 800 and 24 960 cm^{-1}, corresponding to the Cr(III) transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$, respectively. The $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transition is hidden below charge transfer bands. The first of these transitions gives directly the value of 17 800 cm^{-1} for Δ_o in this system. We find 17 010 cm^{-1} for the same transition (of comparable breadth) in our green $Cr(OH)_3$, consistent with the literature value of 17 400 cm^{-1} for $[Cr(H_2O)_6]^{3+}$,[26] and the relative sizes of ligand field splittings by OH^- and H_2O. We infer that the Cr(III) ions are experiencing a more powerful ligand field in the $x = 2$ LDH than in the $Cr(OH)_3$, a shift which we attribute to electronic competition between Cr(III) and the less powerfully electron-attracting Zn(II), affecting the donor ability of bridging OH groups toward the Cr(III) ions. Table 7 compares the observed Cr(III) electronic transitions of Zn(II):Cr(III) LDHs with various Zn(II):Cr(III) ratios.

Titrations involving Cr(III) in the presence of either Mg^{2+} or Mn^{2+} do not yield similar results. Magnesium and chromium chlorides merely yield a mixture of the corresponding hydroxides, rather than a LDH. However, titrating a solution of Mg^{2+} and Cr^{3+} with sulfate as the compensating anion does yield a LDH phase, albeit in a two-step process. This is consistent with existence of Mg(II):Cr(III) LDH carbonates in nature,[9] the synthesis of Mg(II):Cr(III) LDH carbonates in the laboratory,[7] and the greater stability of LDH carbonates and sulfates compared with the corresponding chlorides. The titration curve of Mn^{2+} and Cr^{3+} solutions shows extremely complicated behavior, most likely influenced by oxidation.

The results of this and the accompanying paper[1] show that the relative stabilities of layered double hydroxides and the pH at which they form are related to the stabilities of the corresponding metal hydroxides. For a given M, the lower the solubility of $M(OH)_2$, the lower the pH required to form $[M(II)]_2M(III)(OH)_6X$. This is as expected. For certain systems containing Cr(III), a single-step titration curve is seen, demonstrating direct synthesis of the LDH. Simple calculations, based on pH titration data, may be used to calculate the relative stabilities of various layered double hydroxide systems. Generally, the stability of the LDH, relative to its component ions, increases with the stability of both the trivalent and divalent metal hydroxides. For Cr(III)-containing systems, these trends follow the order already established for Al(III) and Fe(III) systems, namely Mg < Co ≈ Ni < Zn. Unlike the Al and Fe(III) derivatives of ref 1, the LDH systems studied here are more thermodynamically stable than a mixture of the simple hydroxides. For the Al and Fe(III) derivatives, the formation of LDH chlorides by reaction 1 is driven forward under the usual reaction conditions by mass action effects, although, if the disparity between hydroxide and chloride concentrations were smaller, a mixture of the simple hydroxides would be preferred. However, we predict that under strongly alkaline conditions, where hydroxide concentrations begin to approach those of the other ions present, the one-step LDHs discussed in this paper will indeed remain stable relative to the separated hydroxides, in direct contrast to a majority of the systems discussed previously.[1] The most stable phase of all under those circumstances would probably be the LDH hydroxide, since hydroxide is generally preferred to chloride in LDH.[27] We are investigating this possibility.

Relationship to Earlier Work

Since submitting our preliminary publication,[2] we have learned that the titration of mixed Zn(II):Cr(III) and Ni(II):Cr(III) salts with base was previously carried out by de Roy and El Malki et al. (ref 5 and references therein), who interpreted their results in terms of the transient formation of $Cr(OH)_3$. Influenced perhaps by this interpretation, Trifirò and Vaccari[28] assumed that this process was leading to phases of ill-defined composition. The results presented here show that $Cr(OH)_3$ is not a thermodynamically plausible intermediate in these reactions and that well-defined phases may be more accessible than previously realized.

Acknowledgment. We thank the Welch Foundation (Grant B-1154), the University of North Texas Faculty Research Fund, and NASA's Exobiology program (Grant NAGW-4620) for support, and Dr. K. Balkus of the University of Texas at Dallas for obtaining XRD data and for helpful discussions.

CM980524M

---

(21) Bellotto, M.; Rebours, B.; Clause, O.; Lynch, J.; Bazin, D.; Elkaïm, E. *J. Phys. Chem.* **1996**, *100*, 8527.

(22) Serna, C. J.; White, J. L.; Hem, S. L. *Clays Clay Miner.* **1977**, *25*, 384.

(23) Serna, C. J.; Rendon, J. L.; Iglesias, J. E. *Clays Clay Miner.* **1982**, *30*, 180.

(24) Taylor, H. F. W. *Miner. Magn.* **1969**, *37*, 338.

(25) Vucelic, M.; Jones, W.; Moggridge, G. D. *Clays Clay Miner.* **1997**, *45*, 803.

(26) Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1966.

(27) Miyata, S. *Clays Clay Miner* **1983**, *31*, 305.

(28) Trifiró, F.; Vaccari, A. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Macnicol, D. D., Davies, J. E. D., Vogtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 7, p 251.