

## One-Step Formation and Characterization of Zn(II)–Cr(III) Layered Double Hydroxides, $Zn_2Cr(OH)_6X$ ( $X = Cl, 1/2SO_4$ )

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The layered double hydroxides, LDH (Doppelschichtstrukturen, Feitknecht<sup>1,2</sup>), of general formula  $M^{II}_xM^{III}(\text{OH})_{2+2x}Y$  or, as a special case,  $M^{III}_2M^I(\text{OH})_6Y$  have been extensively reviewed<sup>3–7</sup> and were the subject of no fewer than seven publications in *Chemistry of Materials* during 1997.<sup>8–14</sup> One recurrent issue in such papers is the question of order–disorder among the cations, given that very small cation-ordered domains will not be detectable by X-ray diffraction. Another is the development of reproducible preparative techniques, given that all reported preparations presumably involve the precipitation of a monometallic hydroxide and its subsequent conversion into the final product. These facts prompt us to describe our recent finding that one class of LDH can be prepared directly from solution and that there is spectroscopic and thermodynamic evidence for a thermodynamically distinct phase with  $x = 2$  and possible local cation ordering, in at least one member of this class.

(This is in contrast to the reaction of mixed magnesium and aluminum chlorides with alkali at controlled high pH,<sup>15</sup> where LDH is the first material isolated, but it seems probable that  $Al(OH)_3$  is formed as an intermediate in the mixing zone.)

The existence of LDH as distinct phases was established by potentiometric titration as early as 1930<sup>16</sup> and Feitknecht used pH titration to prepare LDHs,<sup>1,2</sup> but until now, this method has been applied to thermody-

Table 1.  $pK_{sp}$  Values for  $M^{II}(\text{OH})_2$  and  $M^{III}(\text{OH})_3$ <sup>20</sup>

ion	Al <sup>3+</sup>	Fe <sup>3+</sup>	Cr <sup>3+</sup>	Mg <sup>2+</sup>	Mn <sup>2+</sup>
$pK_{sp}$	32.90	37.40	30.20	10.74	12.72
ion	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
$pK_{sp}$	15.10	14.80	14.70	19.66	16.92

amic issues for only one rather atypical LDH system,  $Fe^{II}_4Fe^{III}_2(\text{OH})_{12}SO_4$ .<sup>17</sup> For such archetypal LDH as those where  $M(\text{II}) = \text{Mg}$  and  $M(\text{III}) = \text{Al}$  or  $\text{Fe}$ , the formation/pH curve is known to show two plateau regions. The first of these corresponds to the precipitation of  $M(\text{III})$  hydr(ous) oxide, while the second corresponds to progressive conversion of the initial precipitate into LDH. Treadwell and Bernasconi<sup>16</sup> and, later, Turner and Brydon<sup>18</sup> found, for  $M(\text{II}) = \text{Mg}$ , that this plateau is lower than that for the precipitation of  $M^{II}(\text{OH})_2$  itself. We have found this to be generally the case where LDH are formed, and have derived semiquantitative solubility products for LDH from the titration curve in the presence of excess  $M(\text{II})$  ions. The pH of the second plateau decreases when  $M(\text{II})$  hydroxide is of lower solubility, but always increases on going from  $Al(\text{III})$  to  $Fe(\text{III})$ , since in this second reaction the  $M(\text{III})$  hydr(ous) oxide is a reactant, rather than a product.<sup>19</sup>

It therefore occurred to us that if the hydroxide of  $M(\text{II})$  were sufficiently insoluble, while that of  $M(\text{III})$  were sufficiently soluble, the expected position of the “second” plateau of the titration curve could actually fall below that of the first. This would correspond to the *direct*, one-step formation of LDH, without the intermediacy of a single-metal hydroxide phase. Table 1 summarizes the  $pK_{sp}$  values for some of the most common LDH metals, which directed our attention to LDH containing  $Cr(\text{III})$  and the later transition elements. We also reasoned that if distinct LDH phases were formed with different values of  $x$ , this fact should be evident from the titration curve. We therefore performed the titration of mixed zinc chloride/chromium(III) chloride solutions against sodium hydroxide solution, using different Zn:Cr ratios.

All titrations used 250 mL of a solution 0.10 M in  $Cr(\text{III})$  and containing the amount of divalent metal used as determined by the desired solution stoichiometry, with NaCl added to yield an overall 1.0 M chloride concentration. These mixed metal solutions were titrated gravimetrically with certified 50% (w/w) NaOH solution, added in approximately 0.1 g lots, in a 25 °C constant-temperature bath. Solution pH was monitored by a Fisher Accumet 1002 pH meter equipped with automatic temperature compensation capabilities. Addition of base occurred following stabilization of the solution pH, which usually occurred in less than 2 min.

Figure 1 compares the titration curves of 2:1 solutions of Zn(II) with  $Al(\text{III})$ ,  $Fe(\text{III})$ , and  $Cr(\text{III})$ . The Zn:Al and Zn:Fe solutions show the expected two-step LDH formation, while the titration curve of the Zn:Cr solution clearly shows the direct formation of a LDH phase with  $x = 2$ , thermodynamically more stable than  $Cr(\text{III})$

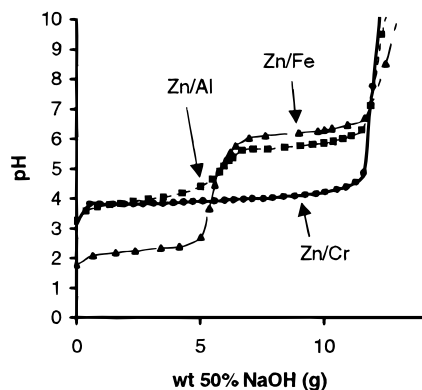
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**Figure 1.** Titration curves of Zn(II):M(III) solutions: ■, Zn:Al; ▲, Zn:Fe; ●, Zn:Cr.

hydroxide itself. The assignment of this material as LDH is further confirmed by its composition, infrared spectrum, powder X-ray diffraction pattern, and facile replacement of chloride by sulfate. Moreover, the precipitate showed throughout the titration the characteristic purple color of Zn/Cr LDH, quite distinct from the greenish color of  $\text{Cr}(\text{OH})_3$ . Powder X-ray diffraction gave basal spacings of 7.8 and 10.7 Å for the chloride and sulfate LDH, respectively, in close agreement with published results.<sup>21,22</sup>

For Zn:Cr 3:1, the titration curve showed two regions; the transition point between these corresponded quantitatively to the formation of material with  $x = 2$ , while the second was in the correct position for the precipitation of  $\text{Zn}(\text{OH})_2$ . Similarly, when the Zn: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  $\text{Cr}(\text{OH})_3$ . However, these findings in 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.

We suggest that the material first formed in these titrations has an ordered local arrangement of Zn(II) and Cr(III) cations, with  $\text{Cr}^{3+}$  in the center of hexagons formed by six  $\text{Zn}^{2+}$  cations, 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 UV-vis diffuse reflection spectrum (Table 2) shows absorption maxima at 17 800 and 24 960  $\text{cm}^{-1}$ , corresponding to the Cr(III) transitions  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\Delta_0)$  and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ , respectively. The  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition is hidden below charge-transfer bands. Gutmann and Müller report 17 900  $\text{cm}^{-1}$  as the  $\Delta_0$  for the corresponding carbonate.<sup>23</sup> We find 17 010  $\text{cm}^{-1}$  for  $\Delta_0$  in our green  $\text{Cr}(\text{OH})_3$ , consistent with the literature

**Table 2.** Diffuse Reflectance UV-Vis Absorption Maxima for Zn/Cr LDHs ( $\text{cm}^{-1}$ )

compound	Zn:Cr	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$	${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$	ref
$\text{Cr}(\text{OH})_3$		17 010	23 660	a
$\text{ZnCr}(\text{OH})_4\text{Cl}$	1.03	17 310	24 180	a
$\text{Zn}_7\text{Cr}_4(\text{OH})_{22}(\text{CO}_3)_2$	1.75	17 480	24 500	23
$\text{Zn}_2\text{Cr}(\text{OH})_6\text{Cl}$	1.97	17 800	24 960	a
$\text{Zn}_2\text{Cr}(\text{OH})_6(\text{CO}_3)_{0.5}$	2.00	17 900	25 570	23
$\text{Zn}_3\text{Cr}(\text{OH})_8\text{Cl}$	3.15	18 040	24 860	a

<sup>a</sup> This work.

value of 17 400  $\text{cm}^{-1}$  for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ <sup>24</sup> and the relative sizes of ligand field splittings by  $\text{OH}^-$  and  $\text{H}_2\text{O}$ . We infer that the Cr(III) ions are experiencing a more powerful ligand field in the  $x = 2$  LDH than in  $\text{Cr}(\text{OH})_3$  and attribute this shift 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. Similar data for the  $x = 3$  and 1 LDH provide  $\Delta_0$  values of 18 040 and 17 310  $\text{cm}^{-1}$ , with no evidence of peak broadening or splitting, strongly indicating that the materials with  $x \neq 2$  are true LDHs and not a mixture of the  $x = 2$  LDH and metal hydroxide. These data further suggest that, within each of these materials, the Cr(III) ions tend to occupy only one kind of site. Thus the data are suggestive of short-range ordering; such ordering has recently been clearly demonstrated<sup>25</sup> in Mg/Fe(III) LDH carbonate. Long-range order is, of course, another matter. Gutmann and Müller have reported similar spectroscopic results for Zn/Cr LDHs prepared from  $[(\text{H}_2\text{O})_4\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{H}_2\text{O})_4]^{4+}$ .<sup>23</sup> The existence of this chromium dimer in LDHs explains the ease with which the Zn/Cr LDHs form with Zn:Cr ratios less than 2, contrary to observed trends for Al- or Fe-containing LDHs.<sup>5</sup>

Co(II), Ni(II), and Cu(II) behave similarly to Zn(II), and the Co:Cr, Ni:Cr, Cu:Cr and Zn:Cr systems all show the expected replacement of chloride by sulfate, confirming their double-layered nature. Among Al-containing LDHs we have examined, only Cu:Al forms directly from solution (as the sulfate). All these materials are being submitted to full spectroscopic, analytical, and X-ray diffraction investigation, and we will be especially concerned to establish whether cation ordering is sufficiently long-range to affect the diffraction signal. In our hands, Mg(II) with Cr(III) does not readily form LDH chloride but does form LDH sulfate, albeit in a two-step process. The Mn(II):Cr(III) system shows more complicated behavior, in addition to interference from atmospheric oxygen, and is under further investigation.

This work has obvious implications for the controlled formation of Zn/Cr catalysts and catalyst supports. In addition, it raises further interesting issues regarding the arrangement of the anions, relevant to the ability of LDH to control the reactivity and photoreactivity of interlayer species,<sup>26,27</sup> a type of supramolecular chemistry of potential importance in areas ranging from industrial catalysis to the origins of life.

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