Hydrotalcites are layered hydroxide materials that form naturally and can be synthesized readily. Their generic formula is $\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2(\text{A}^n)^{-x/n} \cdot n\text{H}_2\text{O}$, in which M(II) indicates divalent metals, M(III) indicates trivalent metals, and A indicates a variety of inorganic or organic anions. The metals and hydroxide groups form a brucite-like layer that is positively charged owing to the presence of trivalent metals; this charge is balanced by interlayer anions, surrounded by water molecules. This description suggests that hydrotalcites are relatively simple chemical systems with systematic and predictable relationships between composition and crystal structure. In fact, hydrotalcites are messy systems, chemically and structurally. Hydrotalcites are solid solutions with compositional limits. Although we would expect limited cation substitution based on differences between M(II) and M(III) radii, those limits have not been predictable from composition. Rather, they have been established empirically only for some of the chemical systems that promote hydrotalcite formation.

We have studied the chemical, crystallographic, and crystal size characteristics of synthetic Co and Al-containing hydrotalcites. Our hydrotalcites were synthesized at three temperatures (25, 45, and 55 °C) and two ionic strengths (0.1 and 1.0 M NaNO3) by a coprecipitation method in aqueous solution. Precipitates remained in their synthesis solutions for 7 days, with interim samples collected 24 hours after reagent addition to the solution was complete. Solution pH was maintained at 9.0 throughout the experiment. All experiments contained the same total Co:Al concentration ratio (3.2) and were exposed to ambient air. Resulting precipitates were analyzed for Co and Al concentration (ICP-AES), crystallographic characteristics (XRD), crystallite size (via interpretation of XRD data) and anion chemistry (EA).

Very few of the chemistry-structure relationships commonly expected for hydrotalcites were observed, although the basic hydrotalcite structure was confirmed by XRD. We expected the larger cation (Co) to force a larger d(110), but we saw no clear relationship between precipitate Co:Al ratio and d(110). We expected the larger charge associated with an Al3+-rich layer to cause greater electrostatic attraction between hydroxide layers and interlayers, yet we saw no trend between precipitate Co:Al ratio and d(003). We expected the flatter carbonate ion (vs. nitrate) to allow a narrower interlayer spacing, yet we saw no correlation between anion chemistry and d(003).

Intended variations in our synthesis conditions apparently did not influence precipitate characteristics significantly. The 7-day aging period affected neither chemistry nor crystallite size. Increased synthesis temperature caused the range of Co:Al ratio values to cluster more than at lower temperature, but it did not affect crystallite size or anion chemistry. Ionic strength did not have a systematic effect on precipitate chemistry or crystallite size.

On the whole, our results suggest that even synthetic, binary hydrotalcites fail to follow systematic relationships between chemistry and structure. In addition, varying the synthesis conditions did not alter the properties of our synthetic hydrotalcites. Combined, these observations suggest that the stability field for hydrotalcites may be larger than previously anticipated, in part because the structure accommodates enough flexibility in composition to allow minor changes without significant structural change. It is possible that we examined systems over too narrow a range of Co:Al to observe the expected relationships, in which case this study enables us to set limits below which the relationships that are in common use for hydrotalcites appear to be insensitive.