

Supporting information for: Kinetic control of intralayer cobalt coordination in layered hydroxides:



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1 High resolution x-ray photoelectron spectroscopy

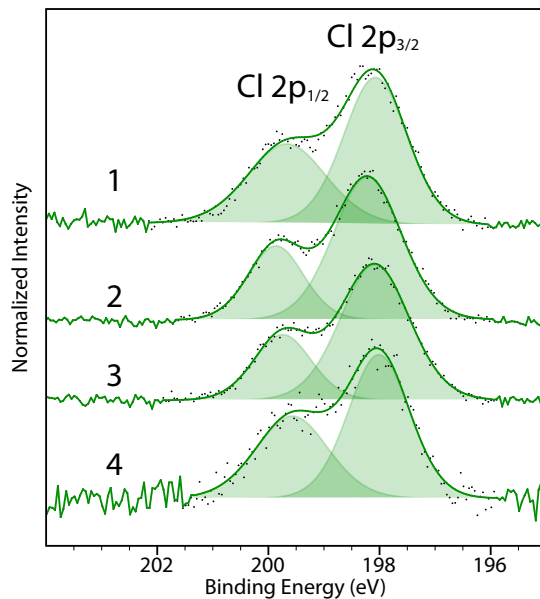


Figure S1: X-ray photoelectron spectra of the Cl $2p$ core levels of compounds **1-4** illustrating the decomposition of each band ($2p_{3/2}$ and $2p_{1/2}$) as one distinct chlorine specie

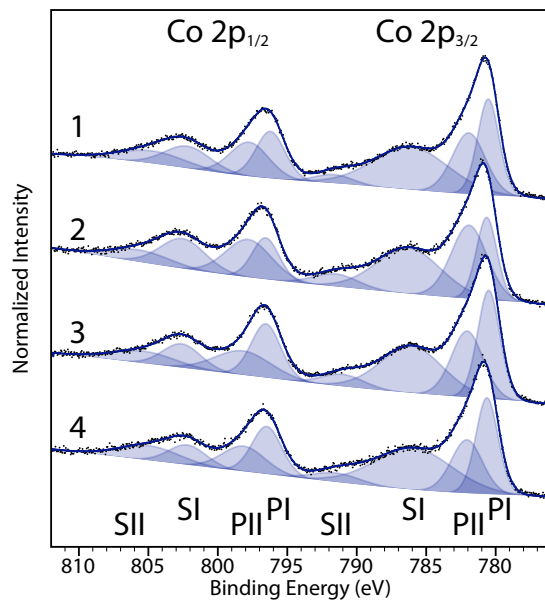


Figure S2: X-ray photoelectron spectra of the Co $2p$ core levels of compounds **1-4** illustrating the decomposition of each band ($2p_{3/2}$ and $2p_{1/2}$) into two distinct cobalt species (I,II) consisting of both parent (P) and satellite (S) peaks from each species. Note the pseudo-arbitrarily chosen background subtraction, bringing large error to peak positions and areas.

Table S1: Summary from decomposition of the Co 2*p* core levels of compounds **1-4** with a pseudo-arbitrarily chosen background (see Figure S2).

Compound	Presumed fraction of Co ^{tet} (by EDS)	Peak area of species I (Co ^{oct})	Peak area of species II (Co ^{tet})
1	33%	60.0%	40.0%
2	40%	54.0%	46.0%
3	27%	59.7%	40.3%
4	23%	61.3%	38.7%

2 Additional structure refinement

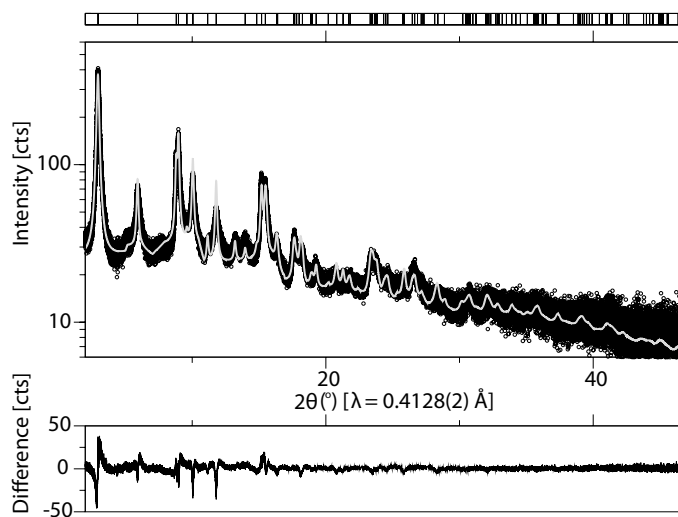


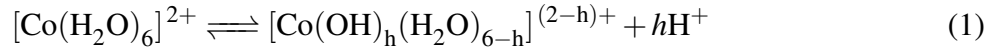
Figure S3: Powder x-ray diffraction (APS, beamline 11-BM at 30 keV) of **4** (black circles) and calculated structure profile (grey line) accompanied by the locations of major diffraction planes (black hashes, top) and difference profile (black line, bottom).

3 Elaboration of the partial charge model, as applied

A partial charge model, as described by Livage et al.,¹ is useful for describing the simple behavior of soluble metal complexes in aqueous solutions. This model assumes that a given complex is stable when the partial charges of bound ligands equal the mean electronegativity of the solution, which is highly pH dependent. Subsequent calculations, based on Allred-Rochow electronegativities, enable prediction of two specific characteristics of soluble metal complexes: the number of associated hydroxyl ligands as a function of pH and the pH range of stable complexation by a soluble counteranion.

3.1 Bound hydroxyls as a function of pH

For a starting solution of $CoCl_2$, which is predominantly formed of cobalt hexaquo complexes,^{2,3} the pH dependent number of bound hydroxyls, h , is defined by the following reaction:



Adapted from Henry et al.,⁴ the sum of partial charges, δ_i , of each element, i , in the hydrolyzed complex must match the complex's total charge to satisfy charge neutrality, and is written as:

$$\delta_{Co} + (6 \cdot \delta_O) + [2(6 - h) \cdot \delta_H] = 2 - h \quad (2)$$

The partial charge of a given element is described by the elemental electronegativity, χ_i^0 , and the mean electronegativity, summed over i elements in the complex of charge z :

$$\chi = \frac{\sum_i (\chi_i^0)^{1/2} + 1.36z}{\sum_i (\chi_i^0)^{-1/2}} \quad (3)$$

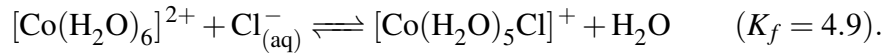
according to the relationship:

$$\delta_i = \frac{\chi - \chi_i^0}{1.36 (\chi_i^0)^{1/2}} \quad (4)$$

The number of associated hydroxyls is then solved as:

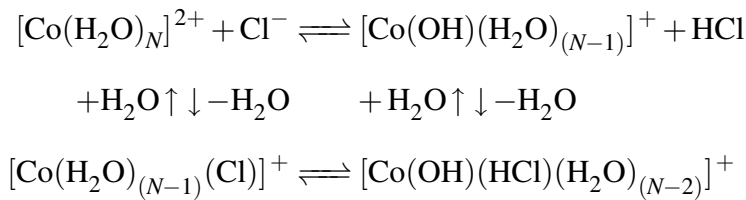
$$h = \frac{2 - \delta_{Co} + 6\delta_O + [(12 - h) \cdot \delta_H]}{1 - \delta_H} \quad (5)$$

This relationship varies with pH since the mean electronegativity of the hydrolyzed complex, χ_h , must follow that of water, $\chi_h = \chi_{\text{water}} = 2.732 - 0.035 \cdot pH$.⁴ The partial charge of each constituent is also dependent on this relationship by definition of the mean electronegativity, requiring recalculation of h for each pH . This relationship is then plotted in Figure 7a to illustrate the pH ranges at which each subsequent hydrolysis reaction occurs ($h > 0$). This analysis, ignoring the Cl^- species, is generally accurate under equilibrium conditions, as the equilibrium complex formation constant is low for the anion association reaction:



3.2 Complexation by anionic species

Since an equilibrium does exist with the counteranion, Cl^- , the additional reactions involving possible complexing reactions must also be considered, according to the partial charge model:⁴



In this equilibrium, there are two pathways for dissociation of the chloride ligand from the cobalt complex with coordination number, N : anionic (upper left), and hydrolytic (upper right). Prediction of the equilibrium state at a given pH requires comparison of the mean electronegativity of

the associated complex, $[\text{Co}(\text{H}_2\text{O})_N(\text{Cl})]^+$ to the mean electronegativity of the q -protonated form of the chloride anion ($q = 0$ for Cl^- , $q = 1$ for HCl). Anionic dissociation occurs when the partial charge of the chloride ligand matches its valancy ($\delta_{\text{Cl}} \leq -1$); this occurs when the $p\text{H}$ dependent mean electronegativity of the associated complex exceeds the mean electronegativity of $\text{Cl}_{(\text{aq})}^-$. Likewise, hydrolytic dissociation occurs when the HCl ligand loses a favorable partial charge ($\delta_{\text{HCl}} \geq 0$) and the mean electronegativity of the associated complex, $[\text{Co}(\text{OH})(\text{HCl})(\text{H}_2\text{O})_{N-2}]^+$, matches the mean electronegativity of the protonated anion ($q = 1$), HCl .

A facile method for tracking the $p\text{H}$ dependence involves location of these boundary conditions in a graph in which the mean anion electronegativity, χ_q , is plotted versus $p\text{H}$ (Figure 7b,c).⁴ The formula describing this relationship is:

$$2.732 - 0.035 \cdot p\text{H} = \frac{\chi_q (\Delta + 5.732 + 2.064q) - 4.071 (3.507 + 2.064q)}{\Delta + (1.408 + 0.507q) \chi_q - (3.507 + 2.064q)} \quad (6)$$

where q is the protonation state of the anion and

$$\Delta = 2 - 2.225N - \left[\frac{(4.71 - \chi_{\text{Co}}^0)}{(1.36 (\chi_{\text{Co}}^0)^{1/2})} \right]. \quad (7)$$

Grey boxes in Figure 7b and c outline the boundary conditions mentioned above. The calculated mean electronegativities, Eqn. (3), for $\text{Cl}_{(\text{aq})}^-$ and HCl are 2.39 and 2.44, respectively. The remaining variable, N , is the coordination number of the complex. When $N = 4$, as for tetrahedral coordination (Figure 7b), chloride can associate with cobalt in the range, $3.8 < p\text{H} < 8.9$. The octahedrally coordinated complex, $N = 6$ (Figure 7c), has a narrower range of $p\text{H}$ stability, from 5.3 to 9.1. Precipitation of a solid in either of these ranges can result in formation of a salt structure.⁴ Since precipitation is likely to occur at a $p\text{H}$ of ~ 4.3 , as shown in Figure 7a described by Eqn. (5), the model predicts that the resulting solid contains some tetrahedral cobalt-chloride complexes rather than all octahedral cobalt complexes.

References

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