Inorg. Chem. **2006**, *45*, 3964–3969

Inorganic Chemistry
Article

Tetrahedral Co(II) Coordination in α-Type Cobalt Hydroxide: Rietveld Refinement and X-ray Absorption Spectroscopy

Renzhi Ma, Zhaoping Liu, Kazunori Takada, Katsutoshi Fukuda, Yasuo Ebina, Yoshio Bando, and Takayoshi Sasaki

Advanced Materials Laboratory, National Institute for Materials Science, Namiki 1−1, Tsukuba, Ibaraki 305-0044, Japan

Received December 9, 2005

We report a Rietveld refinement analysis and X-ray absorption study on a green-color Cl^--intercalated α-type cobalt hydroxide phase. The refinement clearly demonstrated that one-fifth to one-sixth of the Co(II) at octahedral sites was replaced by pairs of tetrahedrally coordinated Co(II) on each side of the hydroxide plane, represented by a structural formula of $[Co^{octa}_{0.828}Co^{tetra}_{0.348}(OH)_2]^{0.348+}Cl_{0.348}\cdot 0.456H_2O$. X-ray absorption spectroscopy also indicated that the divalent cobalt were in local neighboring environments of both octahedral and tetrahedral coordination. Furthermore, UV–vis spectroscopic measurements elucidate the typical green/blue color of an α-type cobalt hydroxide.

Introduction

It is known that cobalt hydroxide can be crystallized into a hexagonal layered structure with two polymorphs: α and β.[1−4] β-$Co(OH)_2$ possesses a brucite-like origin ($a = 3.12$ Å, $c = 4.6$ Å), where octahedra with divalent cobalt cations 6-fold coordinated by hydroxyl ions share edges to produce two-dimensional charge-neutral layers stacked one over the other along the *c* direction without any intercalated species (Figure 1a).[3,4] The β phase exhibits a characteristic pink color. On the other hand, the α phases consists of positively charged layers with anions (CO_3^{2-}, NO_3^-, Cl^-, etc.) and water molecules residing in the gallery to restore charge neutrality.[2,5−7] This causes a substantial expansion in the interlayer spacing (~8 Å), and the color also changes from pink to green/blue. By analogy with the isostructural α- and β-$Ni(OH)_2$, α-type cobalt hydroxide displays more interesting interlayer chemistry and may be more promising for high-performance electrode materials than its β counterpart.[2,8−11] This actually triggered the recent interest in the chemical synthesis of α-cobalt hydroxide, although only poorly or

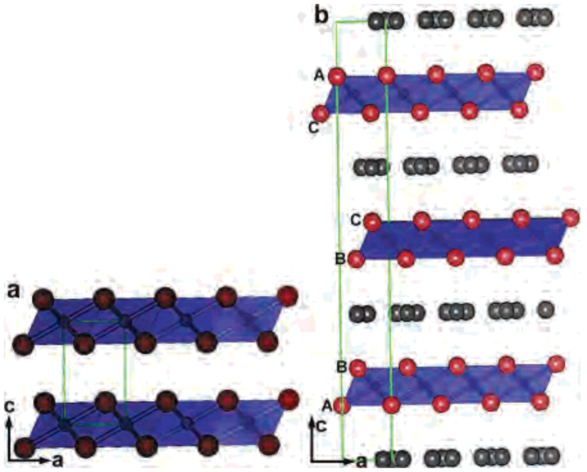

Figure 1. Structure models of (a) β-$Co(OH)_2$ and (b) hydrotalcite-like α-type cobalt hydroxide. Atoms for Co, OH, and guests (interlayer anion, H_2O) are represented by blue, red, gray balls, respectively. In both models, unit cells are indicated by the green rectangles. Labels A, B, and C in model b show the stacking sequence of the hydroxyl.

---

* To whom correspondence should be addressed. E-mail: MA.Renzhi@nims.go.jp.

(1) Bish, D. L.; Livingstore, A. *Miner. Magn.* **1981**, *44*, 339.
(2) Oliva, P.; Leonardi, J.; Laurent, J. F.; Delmas, C.; Braconnier, J. J.; Figlarz, M.; Fievet, F. *J. Power Sources* **1982**, *8*, 299.
(3) Benson, P.; Briggs, G. W. D.; Wynne-Jones, W. F. K. *Electrochim. Acta* **1964**, *9*, 275.
(4) Mockenhaupt, Ch.; Zeiske, Th.; Lutz, H. D. *J. Mol. Struct.* **1998**, *443*, 191.
(5) Rajamathi, M.; Subbanna, G. N.; Kamath, P. V. *J. Mater. Chem.* **1997**, *7*, 2293.
(6) Delahaye-Vidal, A.; Figlarz, M. *J. Appl. Electrochem.* **1987**, *17*, 589.
(7) Rajamathi, M.; Kamath, P. V.; Seshadri, R. *Mater. Research Bull.* **2000**, *35*, 271.
(8) Kamath, P. V.; Dixit, M.; Indira, L.; Shukla, A. K.; Kumar, V. G.; Munichandraiah, N. *J. Electrochem. Soc.* **1994**, *141*, 2956.
(9) Sugimoto, A.; Ishida, S.; Hanawa, K. *J. Electochem. Soc.* **1999**, *146*, 1251.
(10) Bode, H.; Dehmelt, K.; Witte, J. *Electrochim. Acta* **1966**, *11*, 1079.
(11) Singh, D. *J. Electrochem. Soc.* **1998**, *145*, 116.

10.1021/ic052108r CCC: $33.50

turbostratically crystallized aggregates were routinely obtained as a direct result of its metastable feature.[7,12−16]

The structure of α-type cobalt hydroxide is still a matter of debate. There are two possible models to explain the positive charge origin of the $Co(OH)_2$ layers. At first glance, the structure might be analogous to hydrotalcite-like layered double hydroxides (LDH) $[M_1{}^{2+}{}_{1-x}M_2{}^{3+}{}_x(OH)_2]^{x+}$-$[A^{n-}{}_{x/n}\cdot mH_2O]$ (M = metal cation; A = interlayer anion, $CO_3{}^{2-}$, $NO_3{}^-$, Cl^-, etc.), in which positive charge originates from partial substitution of divalent metal cations (Mg, Co, Ni, etc.) by trivalent cations (Al, etc.) in a brucite-like octahedra layer.[17,18] In this regard, α-type cobalt hydroxide may be formulated as $[Co^{2+}{}_{1-x}Co^{3+}{}_x(OH)_2]^{x+}[A^{n-}{}_{x/n}\cdot mH_2O]$ with a mixed valence of Co^{2+}/Co^{3+} in the octahedra layer (Figure 1b). Nevertheless, this model was cast into doubt by experiments claiming that there was no Co^{3+} in the α form.[7,13,19] In fact, the existence of Co^{3+} would impart a gray/black color rather than the green/blue one characteristic of the α-type. Instead, on the basis of the same hydrotalcite-like origin, a partial protonation of the hydroxyl ions into an assumed $[Co^{2+}(OH)_{2-x}(H_2O)_x]^{x+}$ cationic sheet in the absence of Co^{3+} was proposed, even though no solid and direct evidence has been offered to support the hydroxyl deficiency.[13,19] Starting from a hydroxyl vacancy, a guest anion (e.g., $NO_3{}^-$) may be also incorporated into the octahedra layer.[15] Such a direct coordination with the Co cation resulted in a reduced interlayer spacing (∼7 Å). In addition to the above two alternatives, another proposal suggesting the existence of additional Co^{2+} cations at interstitial (tetrahedral) sites was mentioned without detailed interpretation or verification.[19]

Determination of the exact structure of α-type cobalt hydroxide becomes more and more essential to understand and make use of its interlayer chemistry, phase conversion, and electrochemical features. Unlike the hydrotalcite-like LDH structure which has been verified by Rietveld X-ray diffraction (XRD) refinements,[20] the structure of α-cobalt hydroxide has not been clearly determined because the as-prepared samples were always of poor crystallinity, precluding the availability of high quality XRD patterns. Recently, we have successfully synthesized green, uniform, single-crystal hexagonal platelets of Cl^--intercalated α-cobalt hydroxide by homogeneous precipitation from a dilute cobalt chloride solution using hexamethylenetetramine (HMT) as a hydrolysis agent.[21] The reflections in the XRD patterns are not only sharp but also symmetric, distinctly differing from the typical broad "saw-tooth" reflections of the previously reported turbostratic structures of α-type cobalt hydroxide. This feature strongly suggests that they are well-crystallized with a regular interlayer registry, suitable for an accurate Rietveld analysis.

In this study, we attempted to reveal the exact crystal model of α-cobalt hydroxide primarily through a Rietveld procedure. In addition, as the X-ray absorption spectroscopy (XAS) is rich in information relating to valence states and the immediate neighboring environment of the target atoms, X-ray adsorption near-edge structure (XANES) regions at the cobalt K-edge in the as-synthesized product were also examined. For the first time, a tetrahedral coordination is systematically proven in a cobalt hydroxide phase, revealing the long-due structural puzzle.

Experimental Section

Preparation and Chemical Composition. The synthesis was performed in a beaker starting from a dilute aqueous solution of $CoCl_2\cdot 6H_2O$, NaCl, and HMT under an ambient atmosphere as described in ref 21. The green precipitated product was identified as an α-type cobalt hydroxide intercalating Cl^-, water, and a trace amount of carbonate anions. The chemical composition of the as-prepared sample was estimated to be $Co(OH)_{1.70}Cl_{0.26}(CO_3)_{0.02}\cdot 0.56H_2O$. As the carbonate anion was a result of contamination from a slight dissolution of CO_2 from air or possible oxidation of HMT, the composition is reasonably simplified to be $Co(OH)_{1.70}Cl_{0.3}\cdot 0.56H_2O$ to reflect the typical structural feature in this study.

X-ray Powder Diffraction and Rietveld Refinement. XRD data were collected using a Rigaku Rint-2000 Ultima$^+$ diffractometer with graphite-monochromatized Cu Kα radiation (1.5405 Å) in the Bragg−Brentano reflection geometry. Because of the very thin platelet nature of the as-synthesized α-cobalt hydroxide (width = 2−3 μm, thickness = 15 nm), the samples were carefully side-packed into a glass holder to minimize the preferred-orientation effect. The XRD data were measured in a 2θ range from 2 to 120° in steps of 0.02°.

The structure refinements were carried out by the Rietveld and maximum entropy methods (MEM) in an iterative procedure using free software which includes a multipurpose pattern-fitting program, RIETAN-2000,[22,23] and a 3D visualization package, VENUS[24,25] (including VICS, PRIMA, VEND). Specifically, the observed structure factors F_o(Rietveld), estimated from the Rietveld analysis results, were analyzed by MEM to yield three-dimensional (3D) electron densities. F_c(MEM) was thus obtained by the Fourier transformation of the electron densities. Next, the whole pattern fitting to the observed pattern was performed where only the parameters irrelevant to the structure were refined, while the structure factors were fixed at the values of F_c(MEM). The electron density distribution was then determined again by MEM using the values of observed structure factors, F_o, estimated after the whole pattern fitting. In such a manner, MEM analysis and whole pattern fitting were alternately carried out until R factors in the latter no longer decreased appreciably (REMEDY cycles). This is called MEM-based pattern fitting (MPF) and is believed to minimize the

---

(12) Jayashree, R. S.; Kamath, P. V. *J. Mater. Chem.* **1999**, *9*, 961.
(13) Xu, Z. P.; Zeng, H. C. *Chem. Mater.* **1999**, *11*, 67.
(14) Zhu, Y.; Li, H.; Koltypin, Y.; Gedanken, A. *J. Mater. Chem.* **2002**, *12*, 729.
(15) Xu, R.; Zeng, H. C. *Chem. Mater.* **2003**, *15*, 2040.
(16) Barde, F.; Palacin, M.-R.; Beaudoin, B.; Delahaye-Vidal, A.; Tarascon, J. M. *Chem. Mater.* **2004**, *16*, 299.
(17) Allmann, R.; *Acta Crystallogr.* **1968**, *B24*, 972.
(18) Reichle, W. T.; *Solid State Ionics* **1986**, *22*, 135.
(19) Kamath, P. V.; Therese, G. H. A.; Gopalakrishnan, J. *J. Solid. State Chem.* **1997**, *128*, 38.
(20) Bellotto, M.; Rebours, B.; Clause, O.; Lynch, J. *J. Phys. Chem.* **1996**, *100*, 8527.
(21) Liu, Z.; Ma, R.; Osada, M.; Takada, K.; Sasaki, T. *J. Am. Chem. Soc.* **2005**, *127*, 13869.
(22) Izumi, F.; Ikeda, T. *Mater. Sci. Forum* **2000**, *321−324*, 198.
(23) Izumi, F.; Kumazawa, S.; Ikeda, T.; Hu, W. Z.; Yamamoto, A.; Oikawa, K. *Mater. Sci. Forum* **2001**, *378*, 59.
(24) Izumi, F.; Dilanian, R. A. *Recent Research Developments in Physics*; Transworld Research Network: Trivandrum, India, 2002; Vol. 3, Part II.
(25) Izumi, F. *Solid State Ionics* **2004**, *172*, 1.

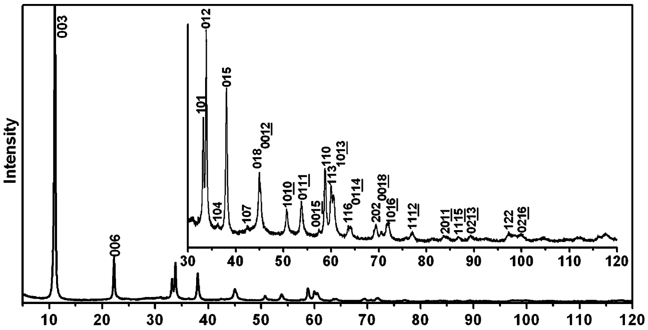

Figure 2. Powder X-ray diffraction pattern for the as-synthesized green α-type cobalt hydroxide. The inset shows a magnification of the high-2θ region. Miller indices for relatively strong Bragg reflections are given.

bias toward the initial structure model.[24,25] VICS and VEND were employed in 3D visualization, rendering, and manipulation of the crystal models and electron-density maps.

X-ray Absorption and UV−vis Spectroscopy. XANES for the Co−K edge were measured at the Photon Factory BL-12C in the Institute of Materials Science, High Energy Accelerator Research Organization (KEK-PF), Japan. The samples were pelleted with BN powders as the binder. Spectra were recorded in transmission mode from 7360 to 8808 eV for the Co edge. UV−vis absorption spectra were recorded in a reflectance mode using a Hitachi U-4000 spectrophotometer.

Results and Discussion

The X-ray powder diffraction pattern of as-prepared Cl^--intercalated α-cobalt hydroxide is shown in Figure 2. Because of the very high aspect ratio of the plateletlike sample, preferred-orientation, represented by the very strong 00*l* reflections, is still notable. Nevertheless, the crystallinity of this compound was high enough to give sharp and symmetric peaks of the *hkl* reflections. From the pattern, a rhombohedral symmetry is first deduced from the systematic extinction of $-h + k + l \neq 3n$. The highly developed hexagonal plateletlike morphology of the product also indicates a hexagonal (rhombohedral) symmetry. The sample was thus refined in $R\bar{3}m$ (No.166) which has the highest symmetry among rhombohedral space groups. With reference to previous reports on the A_xMO_2 family,[26,27] the crystallites may either adopt a possible oxygen atom (herein, hydroxyl) packing of ABBCCA or ABCABC. The former provides trigonal prismatic sites partially occupied by guest anions (P3-type, P = prism) while the latter gives octahedral interlayer sites (O3-type; O = octahedron). Both models belong to $R\bar{3}m$. In our Rietveld refinement, both P3 and O3 hydroxyl packing sequences were taken into consideration. As the O3-type stacking did not attain reasonable convergence, we will only discuss the P3-type packing in the following refinement process.

In the Rietveld procedure, the site occupancies have been initiated according to the previously determined nominal composition of $Co(OH)_{1.70}Cl_{0.3}{\cdot}0.56H_2O$. Atomic scattering factors for the OH ions and H_2O molecules were set to be equal to the sums of those of one oxygen and the corresponding number of hydrogen atoms. A virtual chemical species for the interlayer guests, denoted by M, which has a scattering amplitude equivalent to the mean of those of Cl^- and H_2O, was employed. Isotropic atomic-displacement parameters, *U*, with the isotropic Debye−Waller factor formulated as $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$, were assigned to all the sites. The March−Dollase function and split pseudo-Voigt function were adopted to reflect the possible texture effect (i.e., preferential orientation and anisotropic broadening due to the crystallite-size effect). Since the broad profiles of the reflection in a high 2θ region may decrease the accuracy for the estimation of the intensities, XRD data in the 7−80° region was mainly used in the initial stages of the refinements.

The previously mentioned hydroxyl-deficiency model with a cationic octahedra sheet intercalating chloride anions and water molecules was first adopted to refine the structure. Specifically, Co cations occupy 3*a* (0, 0, 0) sites while OH anions occupy 6*c* (1/3, −1/3, *z*, $z \approx 0.04$) sites. A portion of the water molecules is incorporated into the octahedra layer, sharing 6*c* sites with OH anions. The interlayer guest, M, was constrained near the middle plane 18h (*x*, -*x*, *z*, $z \approx 0.5$). It was compatible with a formula of $[Co(OH)_{1.70}(H_2O)_{0.3}]^{0.3+}$-$[Cl_{0.3}(H_2O)_{0.26}]$. This model yielded the following *R* factors: $R_{wp} = 15.82\%$ ($S = 3.51$), $R_p = 10.33\%$, $R_B = 7.38\%$, and $R_F = 6.78\%$, respectively. The resultant Co−OH bond length was refined as 2.084(4) Å (numbers in parentheses are estimated standard deviations of the last significant digits), comparable to the bond length of 2.043 Å estimated from the Co oxidation state by bond valence calculations. However, the *R* factors appear to be somewhat high. The alternative model, putting chloride anions on the hydroxyl vacant 6*c* (1/3, −1/3, *z*, $z \approx 0.04$) sites and directly coordinating the Co cations into $[Co(OH)_{1.70}Cl_{0.3}]{\cdot}0.56H_2O$, did not lead to any improvement. In addition, 3D electron-density maps determined by MEM always detected electrons with a number density of ∼0.3 $Å^{-3}$ between the octahedra layer and interlayer guest where no actual chemical species are expected to exist in the hydrotalcite-based structure (see Figure 1b). The interstitial positions where the extra electrons were found were situated on 6c (0, 0, *z*, $z \approx 0.07$) sites. The possibilities thus arise that either chloride anions or cobalt cations may occupy the interstitial positions. The interatomic distances between the interstitial site and the octahedral Co(II) and OH^- were estimated to be 1.724 and 1.967 Å, respectively. These atomic distances appear to be too short for an interstitial chloride anion (e.g., an expected value of ∼3.1 Å is needed for Cl^- and OH^-). It therefore seems rational to separate a portion of Co cations from the perfect octahedra layers (3*a* (0, 0, 0)) to produce some tetrahedral sites (6*c* (0, 0, *z*, $z \approx 0.07$).

The proposed tetrahedral Co(II) coordination geometry circumvents the awkward hydroxyl-deficiency assumption. The chloride anions, remaining near the middle plane, directly coordinate with tetrahedral Co(II), forming one tetrahedral apex. The composition may be revised into a corresponding form of $Co_{1.176}(OH)_2Cl_{0.353}{\cdot}0.66H_2O$. The

---

(26) Butel, M.; Gautier, L.; Delmas, C. *Solid State Ionics* **1999**, *122*, 271.
(27) Takada, K.; Sakurai, H.; Takayama-Muromachi, E.; Izumi, F.; Dilanian, R. A.; Sasaki, T. *Adv. Mater.* **2004**, *16*, 1901.

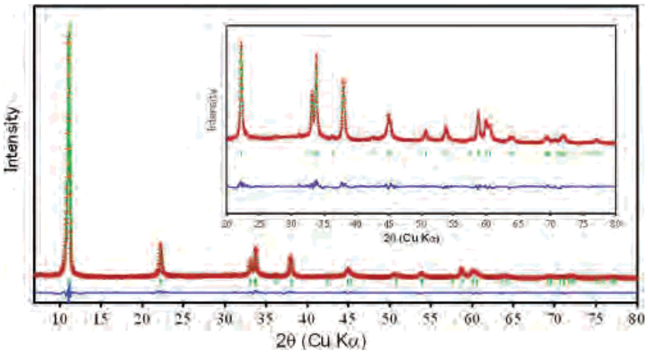

Figure 3. Experimental (red), calculated (solid green line), and difference (blue line near the bottom) XRD patterns using the hydrozincite-like model with a portion of the Co cations occupying tetrahedral sites. Short green vertical bars below the experimental and calculated patterns indicate the positions of allowed Bragg reflections. The inset shows a magnification of the high-2θ region.

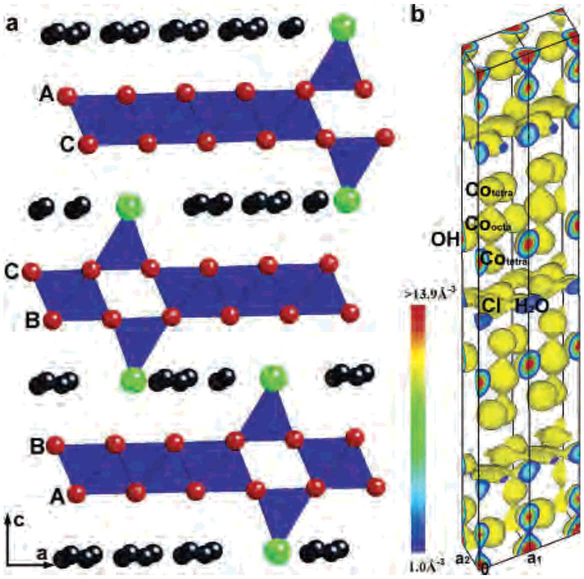

Figure 4. (a) Structural model of $[Co^{octa}_{0.828}Co^{tetra}_{0.348}(OH)_2]^{0.348+}Cl_{0.348}\cdot 0.456H_2O$. Species for Co, OH, Cl, and H_2O are represented by blue, red, green, and black balls, respectively. A, B, and C indicate the stacking sequence of the hydroxyl. (b) 3D electron-density distribution in a 2 × 1 × 1 unit cell. Isosurfaces with an electron density of 1.0 Å^{-3} are displayed. The color scale on the left side indicates electron density on the cross-sections.

Table 1. Structure Parameters for the α-Type Cobalt Hydroxide Showing Fractional Coordinates (*x*, *y*, *z*), Occupancies (*g*) and Isotropic Atomic Displacement Parameters (*U*)[a]

atom	site	*x*	*y*	*z*	*g*	*U* (Å^2)
Co^{octa}	3a	0	0	0	0.828(4)	0.011(1)
Co^{tetra}	6c	0	0	0.0699(3)	0.174[b]	= $U(Co^{octa})$
OH	6c	1/3	−1/3	0.0458(2)	1	0.039(2)
Cl	6c	0	0	0.1680(9)	0.174[c]	0.024(5)
H_2O	18h	0.137(6)	= −$x(H_2O)$	0.500(8)	0.076(4)	= U(Cl)

[a] Space group: $R\bar{3}m$ (No. 166), a = 3.1439(5) Å, c = 24.058(6) Å, R_{wp} = 7.05% (S = 1.56), R_p = 5.45%, R_B = 2.00%, and R_F = 2.42%. [b] $g(Co^{tetra}) = [(1.176 - g(Co^{octa}))]/2$. [b] $g(Cl) = g(Co^{tetra})$.

subsequent refinement appreciably decreased the R factors to R_{wp} = 7.05% (S = 1.56), R_p = 5.45%, R_B = 2.00%, and R_F = 2.42%. In addition to the decrease in R_{wp}, the striking decrease in R_B and R_F evaluated from the observed integrated intensities and structure factors is particularly remarkable. The experimental, calculated, and difference diffraction patterns are shown in Figure 3. A structure model and electron-density distribution map with isosurfaces for an equidensity level of 1.0 Å^{-3} are shown in Figure 4, verifying the validity of the assumption for tetrahedral Co(II) coordination. Even when the pattern-fitting region was extended to 120°, comparable results were still obtained: R_{wp} = 8.08%, R_p = 6.13%, R_B = 2.34%, and R_F = 2.86%.

Fractional coordinates, U parameters, and occupancies are listed in Table 1. The refinements gave a final formula of $[Co^{octa}_{0.828}Co^{tetra}_{0.348}(OH)_2]^{0.348+}Cl_{0.348}\cdot 0.456H_2O$ (Co^{octa} = octahedral Co, Co^{tetra} = tetrahedral Co), consistent with the nominal composition determined by chemical analysis. All the interatomic distances are either close to the values expected by bond valence calculation or reasonable (e.g., octahedra bond length (Co^{octa}−OH) = 2.124(2) Å (expected = 2.043 Å), tetrahedral bond length (Co^{tetra}−OH) = 1.898(2) Å (expected = 1.893 Å), Co^{tetra}−Cl = 2.32(2) Å, Cl−OH = 3.43(2) Å).

The above refinement results revealed some important structural features of the Cl^--intercalated cobalt hydroxide. First, all the Co cations are in a valence state of +2, confirming the absence of Co^{3+}. Second, one-fifth to one-sixth of the octahedral Co(II) sites are vacant. The refinement showed that the tetrahedral Co(II) occupancy was exactly two times that of the octahedral vacancy. This indicates that a pair of Co(II) tetrahedral sites are generated both above and below one octahedral vacancy, sharing three hydroxyl ions with other neighboring octahedra (see Figure 4a). The tetrahedral fourth apex pointing into the interlayer space is occupied by the chloride anion. In Table 1, the isotropic atomic-displacement parameter for the OH site seems to be somewhat high. It might be interpreted that the hydroxyl ions are displaced to some extent from the ideal octahedral coordinating positions because of this sharing effect. Finally, the water molecules are distributed in the gallery, statistically occupying one of six possible 18h sites near the middle plane. The coexistence of octahedral and tetrahedral sites in metal hydroxides was documented early in hydrozincite $Zn_5(OH)_8Cl_2\cdot 2H_2O$ where one-fourth of the Zn(II) at octahedral sites is replaced by pairs of tetrahedrally coordinated Zn(II), giving a structural formula of $[Zn^{octa}_{0.75}Zn^{tetra}_{0.5}(OH)_2]^{0.5+}Cl_{0.5}\cdot 0.5H_2O$.[28,29] It can be concluded that Cl^--intercalated cobalt hydroxide adopts a structure similar to the hydrozincite. The composition also closely matches with that of the early-reported basic cobalt chloride (hydroxysalt) $Co_5(OH)_{8.5}Cl_{1.5}\cdot 2.5H_2O$.[30] In this context, the α-cobalt hydroxide may share the same origin with this hydroxychloride.

In our previous study, it was demonstrated that the Cl^--intercalated cobalt hydroxide showed anion-exchange ability with inorganic (NO_3^-) and organic anions ($C_{12}H_{25}SO_4^-$, DS). However, the substitution reaction hardly proceeded at room temperature and heating conditions were needed.[21] This fact indicated that the chloride anions were exchangeable, although not so easily as counteranions intercalated between

---

(28) Nowacki, W.; Silverman, J. N. *Z. Kristallogr.* **1961**, *115*, 21.
(29) Allmann, R. *Z. Kristallogr.* **1968**, *126*, 417.
(30) Garcia-Martinez, O.; Millan, P.; Rojas, R. M.; Torralvo, M. *J. Mater. Sci.* **1988**, *23*, 1334.

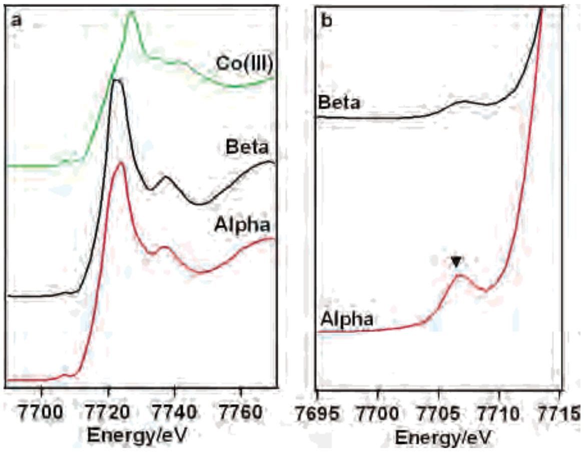

Figure 5. XAS study. (a) XANES of α- and β-Co(OH)$_2$ with Co_2O_3 (Co(III)) as a reference spectrum. (b) The enlarged preedge regions of α- and β-Co(OH)$_2$. The diagnostic preedge peak associated with the 1s → 3d transition is marked (▼). In both spectra, Alpha represents the α-type cobalt hydroxide, while Beta stands for β-Co(OH)$_2$.

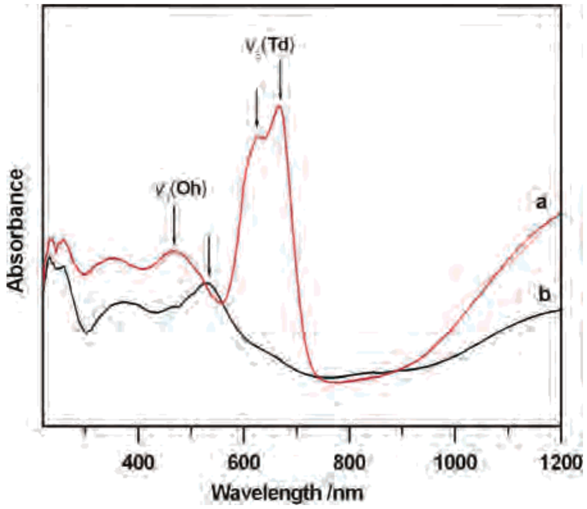

Figure 6. UV−vis diffuse reflectance spectra of (a) α- and (b) β-Co(OH)$_2$. $\nu_3(O_h)$ and $\nu_3(T_d)$ indicate the absorption bands close to the transition energies corresponding to Co(II) in octahedral and tetrahedral coordination, respectively.

octahedra slabs in the hydrotalcite-like structure. Nevertheless, as Cl^- and H_2O actually occupy nearly the same interslab space in the hydrozincite-like model, there is still some room for discussion concerning the exact sites of Cl^- and H_2O. The possibility cannot be excluded that one oxygen of a water molecule might sit on the fourth apex while the chloride anions distribute in the gallery (i.e., swapping the site assignments for Cl^- and H_2O). Such a organization of chemical species has been reported in hydroxynitrate $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ where nitrates are intercalated as counteranions.[31] A nitrate analogue in cobalt with a nominal composition of $Co_7(OH)_{12}(NO_3)_2{\cdot}xH_2O$ was also reported although the structure was not determined.[32] We suspect the possibility that replacement of monatomic Cl^- with NO_3^- or other polyatomic anions such as CO_3^{2-} might generate a miscellaneous structure intermediate between hydrozincite and hydroxynitrate. The refinement by employing intercalated counter chloride anions in our sample produced comparable *R* factors. However, a water content higher than the analytical value, implying a higher electron density, was needed for the tetrahedral H_2O apex. More definite information awaits further studies (such as neutron powder diffraction). In addition, as pairs of tetrahedral Co(II) are situated above and below the empty octahedral sites of the main layer, the ordering of the tetrahedral cations might lead to supercells. Nevertheless, the representative selected-area electron diffraction patterns taken along the [001] zone axis displayed perfect hexagonally arranged in-plane diffraction spots with an estimated lattice constant of $a = 3.1$ Å.[21] It may be understood that the tetrahedral sites are statistically disordered without forming a superstructure.

Figure 5a shows the normalized Co K-edge XANES of the as-synthesized α-type cobalt hydroxide together with β-Co(OH)$_2$. Also included is the spectrum of Co_2O_3 as a reference for Co(III). The edge features of the α-type cobalt hydroxide, strikingly the same as β-Co(OH)$_2$ but distinguishingly different from that of Co(III), indicate beyond doubt the divalent state of cobalt. Moreover, the preedge features of α-type cobalt hydroxide and β-Co(OH)$_2$ were enlarged and compared in Figure 5b. α-Type cobalt hydroxide demonstrates a more intense preedge, a few electronvolts below the K-edge, than that of β-Co(OH)$_2$. This preedge peak results from the absorption process 1s → 3d. The transition probability (peak intensity) is related to the coordination symmetry and to the occupancy of the 3d shell of cobalt.[33] As the cobalt in both compounds are in a divalent state (i.e., a given occupancy), the transition is closely associated with the inversion symmetry of the first coordination shell. In a octahedral (O_h) symmetry, the transition is forbidden by the center of symmetry, even though a weak preedge is actually observed resulting from the crystallographic distortion and constantly vibrating local environments momentarily eliminating the centerosymmetry. This is the case for β-Co(OH)$_2$. In contrast, the preedge peak becomes more intense with the noncentrosymmetric environment of tetrahedral cobalt (T_d). For the α-type cobalt hydroxide, the preedge feature is composed of a portion of tetrahedral contribution and the very weak (forbidden) octahedral contribution, the overall intensity is thus accordingly increased. Therefore, the enhanced preedge features in Figure 5b for the α-type cobalt hydroxide may be interpreted as being more evident for tetrahedral coordination.

The UV−vis measurement also supported the occurrence of tetrahedral Co(II) coordination in the α-type cobalt hydroxide. Figure 6 shows the comparison of UV−vis diffuse reflectance spectra collected on as-prepared α- and β-Co(OH)$_2$. In the visible region, broad absorption bands centered at ∼465 and 530 nm were observed for the α and β phases, respectively. In addition, strong peaks at ∼625 and ∼665 nm were observed only for the α phase. The spectroscopic features for the α-type cobalt hydroxide are in good agreement with the literature showing that the tetrahedron-

---

(31) Stahlin, W.; Oswald, H. R. *Acta Crystallogr.* **1970**, *B26*, 860.

(32) Markov, L.; Petrov, K.; Petkov, V. *Thermochim. Acta* **1986**, *106*, 283.

(33) Moen, A.; Nicholson, D. G.; Rønning, M.; Lamble, G. M.; Lee, J.-F.; Emerich, H. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 4071.

containing cobalt compound typically exhibits peaks at lower energies because of the d−d absorption of Co(II) in tetrahedral coordination geometry.[12,34] The transition energies for the two peaks were calculated to be $\sim 1.5 \times 10^4$ and 1.6×10^4 cm^{-1}, consistent with the reported values for tetrahedral coordination, $\upsilon_3(T_d) = 15\,596$ and $16\,883$ cm^{-1}.[31] This adds clear evidence for the tetrahedral Co(II) coordination in the α-type cobalt hydroxide. For the broad absorption bands, the energies were estimated to be 2.1×10^4 cm^{-1} and 1.9×10^4 cm^{-1} for α and *β*-Co(OH)$_2$, respectively, falling close to the d−d absorption for Co(II) in octahedral coordination, $\upsilon_3(O_h) = 20\,276$ cm^{-1}.[34,35] The spectral features in the visible region, two additional much stronger peaks for α-type cobalt hydroxide, are deemed to be the origin of the green/blue color.

Conclusion

Rietveld analysis of an α-type cobalt hydroxide demonstrated that the Cl$^-$-intercalated phase, with a formula of $[\mathrm{Co^{octa}}_{0.828}\mathrm{Co^{tetra}}_{0.348}(\mathrm{OH})_2]^{0.348+}\mathrm{Cl}_{0.348}\cdot 0.456\mathrm{H_2O}$, was crystallized in such a way that one-fifth to one-sixth of the Co(II) atoms were located at tetrahedral sites formed by brucite hydroxyl and gallery chlorine. The existence of tetrahedral Co(II) coordination was further verified by XAS and UV−vis spectroscopic measurements, indicating the divalent state and explaining the typical green/blue color. Although specific models assuming different locations of the gallery anions might have to be applied for a variety of α-type cobalt hydroxide samples reported in the literature, it points toward the possibility that tetrahedral coordination may be a common feature for the α-type phase.

Acknowledgment. This study was supported by CREST of the Japan Science and Technology Agency (JST).

IC052108R

---

(34) Poul, L.; Jouini, N.; Fievet, F. *Chem. Mater.* **2000**, *12*, 3123.

(35) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: New York, 1984.