

PHYSICAL METHODS
OF INVESTIGATION

Structural Features of Green Cobalt(III) Hydroxide¹

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Abstract—Emission Mössbauer and X-ray absorption XANES/EXAFS spectroscopic techniques are applied to elucidate the structural features of green cobalt(III) hydroxide. A comparative analysis of structurally characterized cobalt(II) and cobalt(III) oxo-compounds shows that the parameters of the local environment of cobalt atoms in green cobalt(III) hydroxide differ substantially from those of its analogues.

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According to several reports [1, 2], the low-temperature reaction of cobalt(II) chloride with hydrogen peroxide in alcoholic media in the presence of sodium hydroxide affords dark green cobalt(II) peroxide. Although this synthesis protocol is broadly recited (in particular, it is described in all editions of the classical manual on inorganic synthesis by N.G. Klyuchnikov starting from 1965 [3–7]), the formation of such a simple cobalt(II) peroxide compound seems hardly possible. Indeed, although there are many compounds with a cobalt atom coordinated to a dioxygen moiety [8–10], this always occurs in mixed-ligand coordination compounds. A dioxygen ligand can be coordinated to either one [11] or two cobalt atoms thus acting as a bridging group in a binuclear compound [12]. In all cases, depending on the specific pattern of the electron density redistribution between the anti-bonding orbitals of the dioxygen ligand and the cobalt π orbitals, these compounds are classified as cobalt(III) and cobalt(III, III) or cobalt(III, IV) peroxo- or superoxo complexes in the cases of mono- and binuclear compounds, respectively [8]. The binding of a peroxo group to a cobalt(II) atom with the d^7 electronic configuration is energetically unfavorable (for instance, see [13]) and, thus, is hardly possible, taking into account the pronounced polarizability and donor properties of the electron pair residing in the anti-bonding orbital of the peroxide group [14]. This suggestion is indirectly supported by our earlier results on similar heavy transition metal dioxygen complexes [15, 16].

We tried to reproduce the described protocol for the synthesis of dark green cobalt(II) peroxide [1–7] and found it to be incorrect [17]. A detailed study using emission Mössbauer spectroscopy [17] unambiguously demonstrated that the reaction product contained cobalt in the oxidation state +3 with no

apparent coordination to a peroxo group. We suggested [17] that this compound was actually a new green modification of cobalt(III) hydroxide. Therefore, the present paper is aimed at the further structural characterization of this compound and in particular at a comparative analysis of structural parameters of the closest coordination environment of the cobalt atoms in structurally characterized cobalt(II) and cobalt(III) hydroxo compounds.

EXPERIMENTAL

The “blue” and “pink” modifications of cobalt(II) hydroxide were synthesized according to standard protocols [7, 18]. These compounds are stable as aqueous slurries under an inert atmosphere but quickly degrade upon drying or in contact with air. In particular, “blue” cobalt(II) hydroxide, if contacted with air, first turns green and then grayish-brown. “Pink” cobalt(II) hydroxide is more stable but also turns grayish-brown upon a prolonged storage. In order to prevent the uncontrolled decomposition, the time delay between the synthesis and characterization with instrumental techniques in the present study was kept as short as possible and carefully sealed wet slurry samples were used. In addition to freshly prepared compounds, aged compounds with colors altered by either prolonged storage or contact with air were also studied.

Cobalt(III) hydroxide was synthesized by the standard method [7, 18] as well as by our own *ad hoc* approach specifically developed to introduce the ⁵⁷Co isotope label into the resultant compound and avoiding the use of bromine. For this, 165 mg of [Co(NH₃)₆]Cl₃ was dissolved in 1 mL of water upon heating. Then, 0.5 mL of 30% hydrogen peroxide, the required amount of ⁵⁷CoCl₂ to achieve an activity of 0.75 mCi; 1 mL of 25% aqueous ammonia; and 2.5 mL of 16 M NaOH were subsequently added to the

¹ The article was translated by the authors.

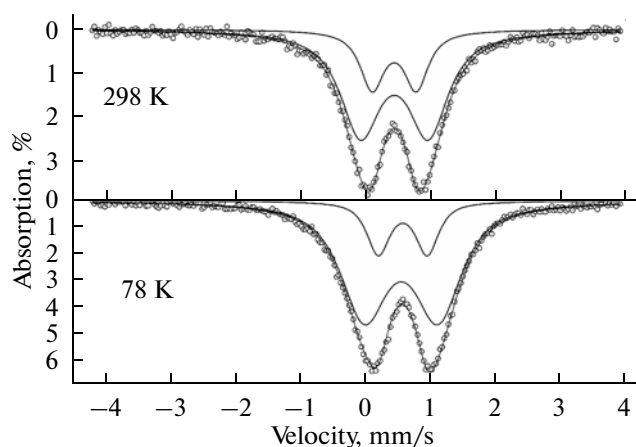


Fig. 1. Deconvolution of emission Mössbauer spectra for green cobalt(III) hydroxide at 78 K and 298 K according to model 1.

solution upon intense stirring. The resultant solution was diluted with water to 5 mL, ozonated for 3 h, and then heated to 100°C for 15 min. The black precipitate formed was centrifuged from the pale mother liquor, and washed first with water to pH 13 and then with acetone. After drying in a vacuum desiccator over CaCl_2 , stable brownish-black powder was afforded.

As it has been established by us earlier [17], the synthesis protocol of dark green cobalt product reported in [1, 2] is incorrect since it implies the presence of trace amounts of carbon dioxide in atmosphere. If all required steps are performed in strictly CO_2 -free atmosphere, brownish-black cobalt(III) hydroxide is always formed [18]. The target dark green compound, i.e., “green cobalt hydroxide,” can be reliably synthesized according to an alternative procedure described in [17]. For this, 10 mL of 30% hydrogen peroxide was added to 20 mL of 4% solution of CoCl_2 (containing the required amount of ^{57}Co corresponding to an activity of 1 mCi) in 96% ethanol precooled to a temperature between -30 and -35°C . The resultant pink solution was cooled back, and 6 mL of 15% aqueous sodium carbonate Na_2CO_3 was dropwise added to it upon intense stirring. The dark green slurry precipitate formed was slowly heated to room temperature avoiding temperature jumps due to the decomposition of excessive hydrogen peroxide. The precipitate was centrifuged from mother liquor and washed subsequently with ethanol and acetone. Finally, the dark green powder was dried in a vacuum desiccator over crystalline potassium hydroxide.

The compound synthesized in this way is stable for at least one month at liquid nitrogen temperature. Meanwhile, at room temperature, its color changes to dark brown within 3–7 days after synthesis.

All reactants used in the synthesis were at least of analytical grade. Cobalt(II) chloride aqueous solution in 0.1 M HCl was used as the ^{57}Co source.

Cooling of the reactants during the syntheses was achieved using a thermostat with aqueous ethylene glycol as a coolant.

Emission Mössbauer spectra were measured using MS1101-E and MS1104EM spectrometers (MOSTEK, Rostov-on-Don, Russia). The measurements were performed both at room temperature and at liquid nitrogen temperature. In both cases, the absorber (potassium hexacyanoferrate(II) characterized by a linewidth of 0.32 mm/s and 29% line intensity for the standard $^{57}\text{Co}/\text{Rh}$ source) was kept at room temperature. The experimental spectra were analyzed by the least-squares method using the appropriate software (Univem MS 9.08, Research Institute of Physics, Southern Federal University, Rostov-on-Don, Russia). All isomer shifts given in the paper are referenced to $\alpha\text{-Fe}$.

The X-ray absorption EXAFS/XANES spectra were measured at the “Structural Materials Science” beamline [19] of the Kurchatov synchrotron radiation source. The measurements were performed in the transmission mode using two gas-tight ionization chambers filled with nitrogen and a 50 : 50 N_2 : Ar mixture for I_0 and I_t , respectively. The samples during measurements were kept in a helium flow at 150 K in order to suppress or decelerate the chemical and structural modification upon contact with atmosphere. The standard data reduction and analysis were performed using the Ifeffit 1.2.11c software suite [20]. The energy scale calibration was achieved by assigning an energy of 7709 eV to the position of the $1s \rightarrow 3d$ pre-edge peak in the experimental spectra.

RESULTS AND DISCUSSION

There are four modifications of cobalt hydroxide, viz., two cobalt(II) hydroxides that are pink and blue and two cobalt(III) hydroxides that are brownish-black and green, the latter being the specific subject of the present paper.

Emission Mössbauer spectroscopy is applied to characterize freshly synthesized green and brownish-black cobalt(III) hydroxides as well as products of their spontaneous decomposition. Some preliminary results on green cobalt hydroxide and its time evolution have been published earlier [17]². In the present paper, more accurate deconvolution parameters for the experimental spectra are reported.

At measured temperatures, the experimental emission Mössbauer spectra of freshly synthesized green cobalt(III) hydroxide feature a well-resolved apparent doublet (Fig. 1), which can be adequately described with a superposition of two nested doublets corresponding to similar isomer shifts (Table 1, model 1). The refined values of isomer shifts for these two partial

² The authors of [17] admitted a numerical error that gave rise to a systematic discrepancy in reported values of the isomer shifts, which however did not affect their basic conclusions.

Table 1. Best-fit parameters of emission Mössbauer spectra for green cobalt(III) hydroxide

Model	<i>T</i> , K	Spectral component no.	Isomer shift δ , mm/s	Quadrupole splitting Δ , mm/s	Linewidth Γ_{exp} , mm/s	Relative area S/S_0 , $\pm 5\%$	χ^2
1	78	1	0.57 ± 0.01	0.75 ± 0.01	0.42 ± 0.09	19	1.3
		2	0.54 ± 0.01	1.13 ± 0.07	0.87 ± 0.13	81	
	298	1	0.44 ± 0.01	0.68 ± 0.02	0.44 ± 0.04	26	1.1
		2	0.44 ± 0.01	1.04 ± 0.02	0.74 ± 0.03	74	
2	78	1	0.46 ± 0.01		2.52 ± 0.05	38	2.9
		2	0.56 ± 0.01	1.00 ± 0.01	0.69 ± 0.01	62	
	298	1	0.44 ± 0.02		2.25 ± 0.07	36	1.5
		2	0.44 ± 0.01	0.90 ± 0.01	0.61 ± 0.01	64	

Table 2. Best-fit parameters of emission Mössbauer spectra for brownish-black cobalt(III) hydroxide

Model	<i>T</i> , K	Spectral component no.	Isomer shift δ , mm/s	Quadrupole splitting Δ , mm/s	Linewidth Γ_{exp} , mm/s	Relative area S/S_0 , $\pm 5\%$	χ^2
1	78	1	0.51 ± 0.01	0.75 ± 0.01	0.43 ± 0.03	27	1.1
		2	0.44 ± 0.01	1.03 ± 0.04	1.18 ± 0.04	73	
	298	1	0.39 ± 0.01	0.75 ± 0.01	0.60 ± 0.01	62	1.8
		2	0.44 ± 0.01	1.54 ± 0.06	1.80 ± 0.08	38	
2	78	1	0.44 ± 0.01		2.10 ± 0.03	68	1.7
		2	0.51 ± 0.01	0.84 ± 0.01	0.50 ± 0.02	32	
	298	1	0.37 ± 0.01		2.42 ± 0.04	59	2.0
		2	0.40 ± 0.01	0.79 ± 0.01	0.53 ± 0.01	41	

doublets correspond to iron atoms (and, respectively, to mother cobalt atoms) in the charge state +3 and in the octahedral coordination by oxygen atoms [21]. Nevertheless, these two doublets differ from each other in the quadrupole splitting and linewidths. Therefore, we assume that these partial components are due to chemically identical configurations of mother cobalt atoms, which occur in differently ordered environments. More specifically, the doublet with a smaller quadrupole splitting and smaller linewidths should correspond to atoms within a well long-range ordered crystalline lattice. Meanwhile, the doublet with a larger quadrupole splitting and broader linewidths corresponds to atoms either in amorphous parts of the sample or in surface regions of crystalline grains. Taking into account non-equilibrium synthesis conditions, the resultant compound is expected to be highly defective, which is in agreement with X-ray diffraction data (X-ray diffraction patterns of the compound always feature only weak and broad peaks).

In the case of brownish-black cobalt(III) hydroxide synthesized via the ozonation of alkaline solutions of hexaaminocobalt(III) chloride, the experimental emission Mössbauer spectra feature a well resolved slightly asymmetric doublet, which can be described as a superposition of two doublets (Table 2, model 1). A few differences as compared to the aforementioned

green cobalt(III) hydroxide are worth noting. First of all, the fraction of well-ordered iron (or mother cobalt) atoms (that are characterized by smaller quadrupole splitting and linewidths) is larger than the fraction of disordered ones (that are characterized by larger quadrupole splitting and linewidths). Furthermore, the isomer shift of the ordered component determined from the room-temperature spectrum differs by 0.05 mm/s from the respective values for the disordered component and both doublets of green hydroxide, and this difference exceeds the nominal accuracy of this experimental parameter. When we try to deconvolve liquid-nitrogen spectra within the same model as a superposition of two doublets, the ratio of areas of spectral components corresponding to the ordered and disordered phases changes. Furthermore, parameters of the disordered phase demonstrate an atypical temperature dependence: the isomer shift does not change, whereas the quadrupole splitting decreases (see Table 2, model 1). These experimental observations imply that either the compound under study experiences a phase transition between room temperature and liquid nitrogen temperature, or the spectral deconvolution model used is inadequate.

In order to reconcile the above discrepancies within the spectral deconvolution model 1, we propose another model assuming a superposition of the dou-

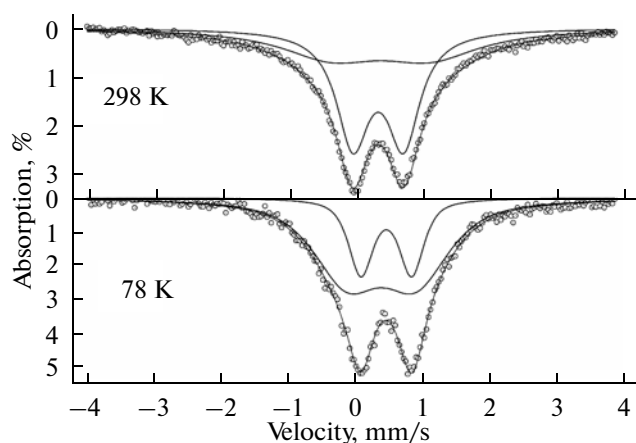


Fig. 2. Deconvolution of emission Mössbauer spectra for brownish-black cobalt(III) hydroxide at 78 K and 298 K according to model 1.

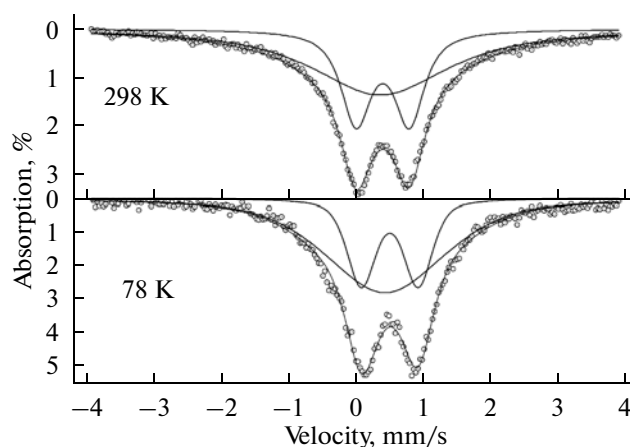


Fig. 3. Deconvolution of emission Mössbauer spectra for brownish-black cobalt(III) hydroxide at 78 K and 298 K according to model 2.

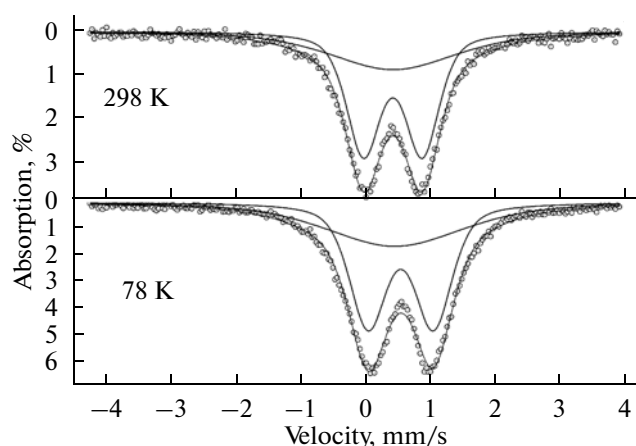


Fig. 4. Deconvolution of emission Mössbauer spectra for green cobalt(III) hydroxide at 78 K and 298 K according to model 2.

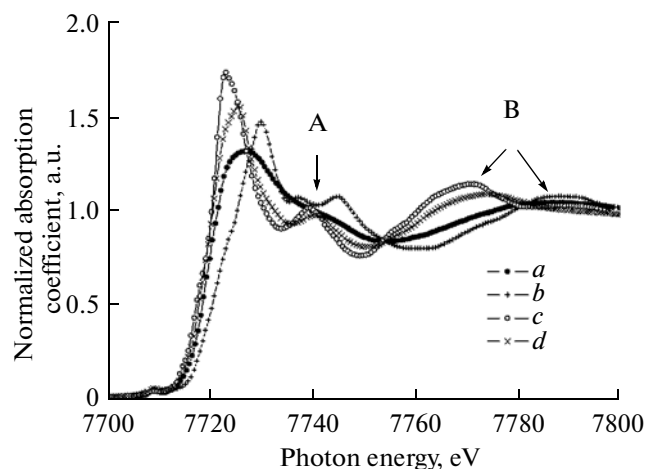


Fig. 5. Co K-edge XANES spectra for the series of cobalt hydroxides: (a) green $\text{Co}(\text{OH})_3$; (b) brownish-black $\text{Co}(\text{OH})_3$; (c) pink $\text{Co}(\text{OH})_2$; (d) blue $\text{Co}(\text{OH})_2$.

blet of the ordered phase and a broad singlet that can be of the relaxation origin (Table 2, model 2; Fig. 3).

The use of such a model (a singlet plus a doublet) for the deconvolution of the emission Mössbauer spectra for green cobalt(III) hydroxide (Table 1, model 2; Fig. 5) affords a statistically less reliable description as compared to model 1 (see Table 1), but the self-consistency of the spectral deconvolution enables a direct comparison of the best-fit Mössbauer parameters for the two cobalt compounds (cf. Table 1, model 2 and Table 2, model 2). It becomes evident that both the isomer shift and quadrupole splitting are larger for green cobalt(III) hydroxide than for brownish-black cobalt(III) hydroxide at all temperatures studied, which implies that there are systematic differences in the local environment of iron (and, respectively, mother cobalt) atoms in these two compounds. More specifically, a larger isomer shift value means an

increased electron density on the metal atom. Meanwhile, a larger quadrupole shift indicates a lower symmetry of the coordination environment. Such a combination of factors can indicate shortened cobalt-oxygen bonds in green cobalt hydroxide(III) as compared to brownish-black one, which is further supported by EXAFS data (see below).

X-ray absorption spectroscopy was used to compare systematically the local environment of cobalt atoms in green cobalt hydroxide and a set of closely related compounds, including brownish-black cobalt(III) hydroxide along with pink and blue cobalt(II) hydroxides.

X-ray absorption near-edge (or XANES) spectra for the samples studied are shown in Fig. 5. The spectrum for green cobalt(III) hydroxide differs significantly from the spectra of reference samples. Indeed, the spectrum is characterized by a more smeared fine

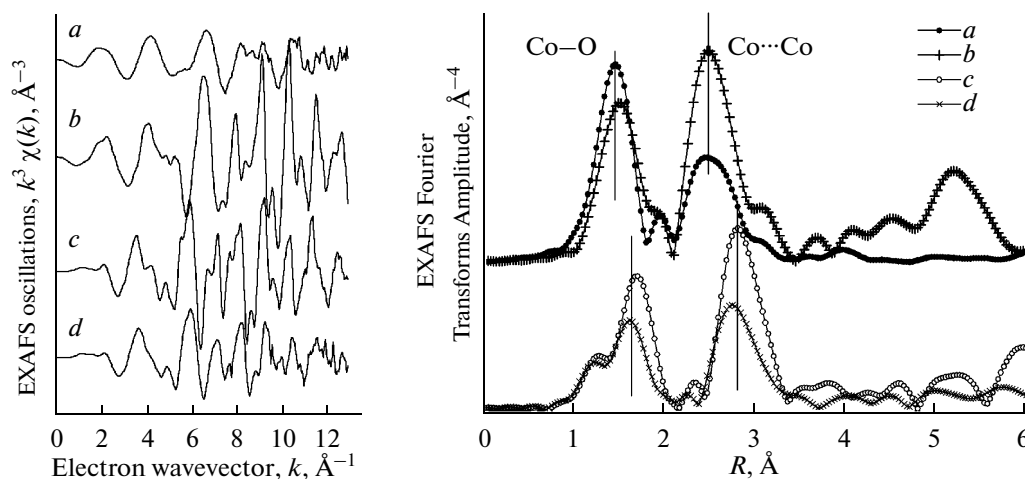


Fig. 6. Co K-edge EXAFS oscillations (left panel) and their Fourier transforms (right panel) for the series of cobalt hydroxides: (a) green $\text{Co}(\text{OH})_3$, (b) brownish-black $\text{Co}(\text{OH})_3$, (c) pink $\text{Co}(\text{OH})_2$, and (d) blue $\text{Co}(\text{OH})_2$ (For clarity, positions of the Co–O and Co···Co coordination spheres are marked, the Fourier transform for green cobalt(III) hydroxide is multiplied by 2.).

structure as compared to all references used, which indicates a lower symmetry and heavier disorder in the local environment of Co atoms therein. At that, the exact position of the absorption edge (which correlates with the oxidation state of the atom being probed) takes an intermediate place between Co(II) and Co(III) reference compounds. The spectra of all samples are characteristic of the electronic transitions and geometric parameters of the atom being excited. The XANES spectrum for brownish-black cobalt(III) hydroxide features a distinct spectral feature “A” at around 7740 eV (Fig. 5), which is absent in the spectra of other reference compounds. In the XANES spectrum for green cobalt(III) hydroxide, such a feature is visible but strongly smeared, which makes it dissimilar to all other reference spectra under consideration. The energy positions of spectral features “B” (Fig. 5) are common for both (green and brownish-black) cobalt(III) hydroxides.

The oscillatory parts of Co K-edge EXAFS spectra and their derived Fourier transforms are shown in Fig. 6. Peaks observed in the EXAFS Fourier transform can be associated with specific coordination spheres around the Co atoms in a sample studied. As it becomes apparent already from visual comparison of the Fourier transforms, peak positions in the FT for green cobalt(III) hydroxide are rather similar to those for brownish-black cobalt(III) hydroxide and distinctly different from both modifications of cobalt(II) hydroxides. Shorter cobalt–oxygen distances in the first coordination sphere are evidently due to the smaller ionic radius of Co^{3+} with respect to Co^{2+} . However, the difference between green and brownish-black cobalt(III) hydroxides is of particular note. FT peaks in the case of the green modification are characterized by significantly lower intensities (Fig. 6). Fur-

thermore, the relative intensity of the second-coordination-sphere peak is additionally attenuated, whereas peaks of longer-distance coordination spheres are nearly completely suppressed. This clearly indicates a pronounced local-structure disorder therein, which is in accord with the above conclusion from XANES spectroscopy.

A full quantitative analysis of the EXAFS spectra includes a non-linear fit of a theoretical model spectrum to the experimental one. As a raw structural model to be refined, we used available crystallographic data for brownish-black cobalt(III) hydroxide [22] and pink cobalt(II) hydroxide [23]. Structural parameters of first two coordination spheres were refined in the non-linear fitting procedure. The first coordination sphere in all cobalt hydroxides is constituted of six oxygen atoms, whereas the second coordination sphere includes six Co atoms within the Co–O–Co atomic chains; the respective photoelectron scattering paths dominate in the experimental EXAFS spectra. Due to the aforementioned difference in ionic radii, the interatomic distances corresponding to these coordination shells are substantially different for cobalt(II) and cobalt(III) hydroxides.

Interatomic distances for the first two coordination spheres along with Debye–Waller factors (that encompassed both atomic thermal motion amplitudes and structurally imposed static scatter in interatomic distances within a coordination sphere) were used as variable parameters in the fitting procedure. Additionally, the Fermi energy shift and the amplitude reduction factor (that takes into account a non-zero probability of multielectron excitations) were refined under assumption that they were equal for all scattering paths for one sample. The best-fit values for variable structural parameters are listed in Table 3. For reference

Table 3. Best-fit local structure parameters according to EXAFS spectroscopy

Sample	R_f , %	Amplitude reduction factor, energy shift, eV	Scattering path	Coordination number	Interatomic distance R , Å	Debye–Waller factor, $\sigma^2 \times 10^{-3}$, Å ²
Cobalt(III) hydroxide–green	1.5	$S_2 = 0.56(6)$, $e_0 = -3.7(1.6)$	Co–O	6	1.893(7)	5.2 ± 0.9
			Co–Co ₁	3.9(6)	2.806(8)	8 ± 2
			Co–Co ₂	2.1(6)	3.087(8)	6 ± 2
Cobalt(III) hydroxide–brownish-black	0.55	$S_2 = 0.70(4)$, $e_0 = -1.1(8)$	Co–O	6	1.901(4)	2.9 ± 0.3
			Co–Co	6	2.854(3)	2.5 ± 0.4
Cobalt(II) hydroxide–pink	1.9	$S_2 = 0.94(8)$, $e_0 = 2(1)$	Co–O	6	2.105(7)	5.5 ± 0.9
			Co–Co	6	3.176(6)	4.7 ± 0.5
Cobalt(II) hydroxide–blue	3.9	$S_2 = 0.93(13)$, $e_0 = 1.6(1.5)$	Co–O	6	2.082(13)	10 ± 2
			Co–Co	6	3.135(10)	8 ± 1

compounds with known structures (i.e., brownish-black cobalt(III) hydroxide and two modifications of cobalt(II) hydroxides), the EXAFS local-structure parameters are in a good agreement with the literature crystallographic data. It is important that no significant change is detected for aged cobalt(II) hydroxides that underwent color alternation upon a prolonged storage or contact with air apart from a slight increase in the ordering degree as manifested in smaller Debye–Waller factors.

In order to get an adequate fit of the EXAFS spectrum for green cobalt(III) hydroxide, we had to use a more sophisticated model of the local environment of Co atoms. The second coordination sphere has to be split into two components with coordination numbers of four and two and noticeably different Co–Co distances. The best-fit values for the Co–Co distances differ significantly from all other cobalt reference hydroxides, and thus they can be regarded as specific structural characteristics of green cobalt(III) hydroxide. The cobalt–oxygen interatomic distance for the sample is equal to the respective distance in brownish-black cobalt(III) hydroxide within the error bar, which is fully consistent with the oxidation state +3, since cobalt(II) reference compounds are characterized by much longer Co–O distances. The Debye–Waller factors in the case of green cobalt(III) hydroxide are larger than for brownish-black cobalt(III) hydroxide, which is consistent with a strong local-structure disorder and the lack of long-range crystalline order.

In order to rationalize the observed local-structure disorder, we considered some models implying the introduction of carbonate anions into the coordination environment of Co atoms. Basic cobalt(II) carbonate $\text{CoCO}_3(\text{Co}(\text{OH})_x(\text{H}_2\text{O})_y)$ and cobalt(II) carbonate CoCO_3 [24] were used as structural prototypes. In this case, in addition to Co–O' and Co···Co single-scattering paths, Co···C, Co···O", and multiple Co–O'–C–O" scattering paths were included into the structural model to be refined. Despite the more sophisticated character of the model and difficulties in

differentiating light elements within the second coordination sphere, the “carbonate” model was decisively ruled out.

Therefore, EXAFS spectroscopy data indicate that cobalt atoms in green cobalt hydroxide are characterized by the oxidation state +3 and strongly disordered local structure, which is manifested in a smeared XANES fine structure and large EXAFS Debye–Waller factors. Furthermore, there is a strong experimental evidence that the Co–Co second coordination sphere is split into two components composed of four and two Co atoms at distances of 2.81 Å and 3.09 Å, respectively. This is not typical of other structurally characterized cobalt hydroxides.

CONCLUSIONS

In summary, a consistent comparative analysis of emission Mössbauer and EXAFS/XANES spectroscopy data for all known cobalt(II) and cobalt(III) hydroxo compounds show a substantial difference between the structural parameters of the closest coordination spheres of Co atoms in green cobalt(III) hydroxide from those of its analogues. The distinctive structural features of this compound include: shortened Co–O interatomic distances within the first coordination sphere; a larger electric field gradient and higher electron density on Co atoms with respect to brownish-black $\text{Co}(\text{OH})_3$; the splitting of the Co–Co second coordination sphere into two components. In overall, green cobalt(III) hydroxide is less ordered than brownish-black cobalt(III) hydroxide.

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