



A quarter of a century after its synthesis and with >200 papers based on its use, ' $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$ ' proves to be $\text{Co}_6(\text{CO}_3)_2(\text{OH})_8\cdot \text{H}_2\text{O}$ from synchrotron powder diffraction data

Prateek Bhojane, Armel Le Bail and Parasharam M. Shirage

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A quarter of a century after its synthesis and with >200 papers based on its use, 'Co(CO₃)_{0.5}(OH)·0.11H₂O' proves to be Co₆(CO₃)₂(OH)₈·H₂O from synchrotron powder diffraction data

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The successful attempt to solve the crystal structure of Co(CO₃)_{0.5}(OH)·0.11H₂O (denoted **CCH**), based on synchrotron powder diffraction data, leads to a drastic revision of the chemical formula to Co₆(CO₃)₂(OH)₈·H₂O [hexacobalt(II) bis(carbonate) octahydroxide monohydrate] and to a hexagonal cell instead of the orthorhombic cell suggested previously [Porta *et al.* (1992). *J. Chem. Soc. Faraday Trans.* **88**, 311–319]. This results in a new structure-type related to malachite involving infinite chains of [CoO₆] octahedra sharing edges along a short *c* axis, delimiting tunnels having a three-branched star section. All reports discussing cobalt hydroxycarbonates (**CCH**) without any structural knowledge and especially its topotactic decomposition into Co₃O₄ have, as a result, to be reconsidered.

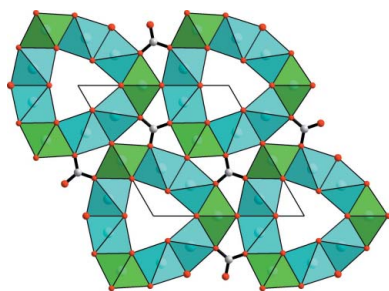
1. Introduction

Since 2010, more than 200 papers have cited Co(CO₃)_{0.5}(OH)·0.11H₂O (formula frequently included in the title), denoted for short **CCH**, as being a precursor of textured and mesoporous Co₃O₄ applied as the electrode material for supercapacitors and lithium-ion batteries (see, for example, Wang *et al.*, 2010*b*; Xiong *et al.*, 2012). An orthorhombic cell was originally proposed (Porta *et al.*, 1992), but was never confirmed by any structure determination and was considered to be correct until now. Owing to the absence of a single crystal of suitable size, a powder diffraction pattern was recorded at the Indian synchrotron facility. The orthorhombic cell, being also in the JCPDS card 48-0083 (PDF, 2012), was ruled out by a quite deceiving Le Bail fit (Le Bail, 2005). Thus, it appeared timely to try to characterize crystallographically this challenging compound.

2. Experimental

2.1. Synthesis and crystallization

The direct-growth binder-free technique was adopted using a simple fast inexpensive and facile hydrothermal method for the fabrication of the nanomaterial on an Ni-foam substrate. In brief, 5 mM Co(NO₃)₂·6H₂O, 0.5 M urea and 10 mM NH₄Cl were dissolved in deionized water (50 ml) and stirred for 30 min to obtain a homogeneous mixture. The resulting light-pink solution was transferred into a 100 ml Teflon-lined stainless steel autoclave. For the direct growth, a few (3–4) pieces of the Ni-foam substrate (1 × 1 cm) were immersed in



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Table 1

Experimental details.

Crystal data	
Chemical formula	$\text{Co}_6(\text{CO}_3)_2(\text{OH})_8 \cdot \text{H}_2\text{O}$
M_r	627.69
Crystal system, space group	Hexagonal, $P\bar{6}2m$
Temperature (K)	293
a, c (Å)	10.3236 (4), 3.12244 (15)
V (Å ³)	288.20 (2)
Z	1
Radiation type	Synchrotron, $\lambda = 0.807700$ Å
μ (mm ⁻¹)	12.06
Specimen shape, size (mm)	Cylinder, 0.5 × 0.5
Data collection	
Diffractometer	MAR345dif
Specimen mounting	Quartz capillary
Data collection mode	Transmission
Scan method	Step
2θ values (°)	$2\theta_{\min} = 3.883$, $2\theta_{\max} = 58.870$, $2\theta_{\text{step}} = 0.020$
Refinement	
R factors and goodness of fit	$R_p = 3.714$, $R_{\text{wp}} = 4.827$, $R_{\text{exp}} =$ 2.465 , $R_{\text{Bragg}} = 3.948$, $\chi^2 = 3.833$
No. of parameters	50
H-atom treatment	H-atom parameters not refined

Computer programs: *McMaille* (Le Bail, 2004), *ESPOIR* (Le Bail, 2001), *FULLPROF* (Rodríguez-Carvajal, 1993), *DIAMOND* (Brandenburg, 1999) and *pubCIF* (Westrip, 2010).

the reaction chamber. Before using the Ni-foam, it was cleaned with 3 M HCl for 10 min. It was then cleaned ultrasonically with ethanol, acetone and distilled water to remove impurities and oxide layers from the surface, and allowed to dry completely. The autoclave was sealed and held at 383 K for 5 h in a muffle furnace, after which it was allowed to cool to room temperature. Finally, we retrieved the Ni-foams, which were found to be coated with a light-purple/pink colour (**CCH**), and the excess precipitate was filtered off using Whatman filter paper, followed by repetitive rinsing with distilled water and ethanol. The effective mass loading on the Ni-foam before and after the hydrothermal treatment was estimated to be 0.2 mg of **CCH**. The compound was identified as corresponding to the previously described ' $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ ' (Porta *et al.*, 1992). The source for both carbonate and hydroxide in the final compound is urea.

2.2. Structure solution and refinement

Angle-dispersive X-ray diffraction measurements were performed at beamline BL-12 of the Indus-2 synchrotron radiation facility [Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India] using an image-plate area detector (MAR345dif) in transmission mode at a wavelength of $\lambda = 0.8077$ Å. In spite of strong peak broadening due to the nanosized particles, the powder diffraction pattern indexing was undertaken through the *McMaille* software (Le Bail, 2004), proposing a hexagonal cell with a short c axis. There are 16 possible space groups, since no systematic extinction was observed. The intensities were extracted using the *FULLPROF* Rietveld software (Rodríguez-Carvajal, 1993; Rietveld, 1969) in Le Bail fitting mode (Le Bail, 2005). Structure solu-

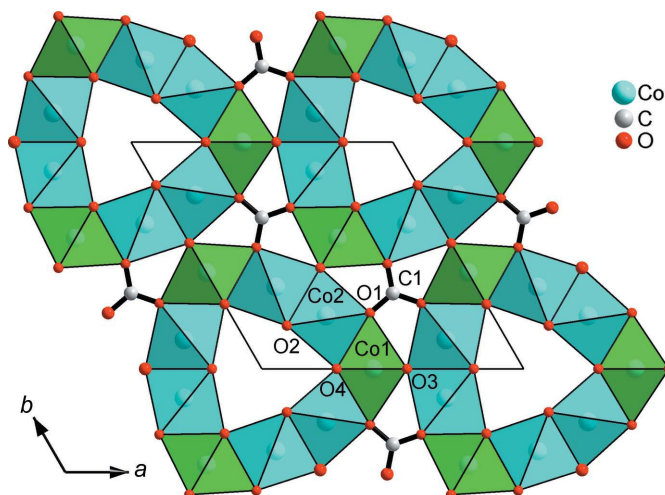


Figure 1

Unit-cell projection of the $\text{Co}_6(\text{CO}_3)_2(\text{OH})_8 \cdot \text{H}_2\text{O}$ structure along the short c axis, showing the rings of nine $[\text{CoO}_6]$ octahedra connected either by edges or faces (three of them are empty, *i.e.* half of the Co2 atoms in blue, avoiding face-sharing), forming tunnels along c .

tion was attempted in direct space using the *ESPOIR* software (Le Bail, 2001). Models leading to R factors as low as 10% were obtained in the space groups $P3$ and $P31m$, trying first the low-symmetry trigonal space groups. At this stage, one Co site was identified as forming $[\text{CoO}_6]$ octahedra connected by edges to form chains along the c axis, interconnected by CO_3 groups. During Rietveld refinements in the space group $P31m$, it became obvious that one atom site had been wrongly attributed to an O atom since it was at the centre of an octahedron so that it could correspond to a second Co atom site, though half occupied (a full occupation would lead to face-sharing octahedra with a very short Co–Co interatomic distance of 2.29 Å). The model was checked for higher symmetry using the *PLATON* software (Spek, 2009) and the space group $P\bar{6}2m$ was suggested and confirmed by further Rietveld refinements. Trying to refine the Co2 atom site occupancy led to a value of 0.47, slightly less than 0.50, but this had no significant effect on the R factors. H atoms could not be

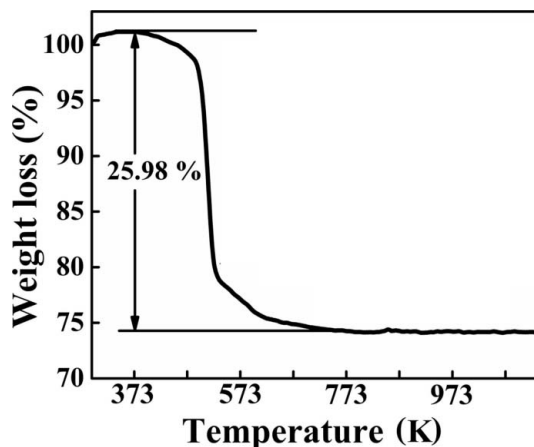


Figure 2

The TGA plot for **CCH**.

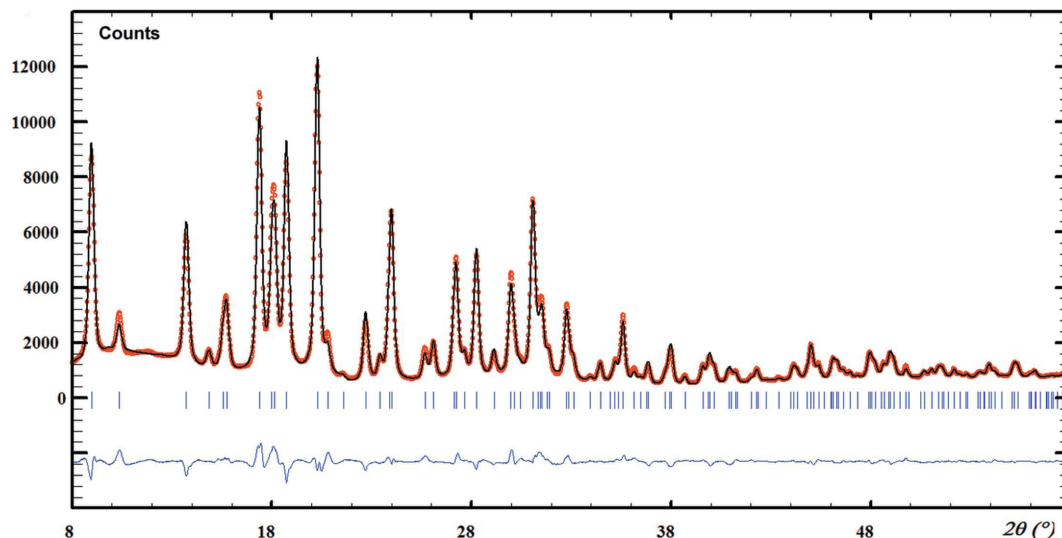


Figure 3

Refined diffraction pattern from synchrotron data for $\text{Co}_6(\text{CO}_3)_2(\text{OH})_8\cdot\text{H}_2\text{O}$. Red dots represent the observed data and the black line represents the calculated pattern. Bragg ticks are the peak positions and the blue curve shows the difference between the observed and calculated patterns. The first reflection (*i.e.* 100) at a very low angle has been excluded for being too close to the beam stop.

located. Therefore, the chemical composition, defined in the 48-0083 JCPDS card to be $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})\cdot 0.11\text{H}_2\text{O}$, has to be changed to $\text{Co}_6(\text{CO}_3)_2(\text{OH},\text{H}_2\text{O})_9$. Cobalt cations being Co^{2+} would mean eight OH^- anions and one water molecule, leading to the alternative formula $\text{Co}_6(\text{CO}_3)_2(\text{OH})_8\cdot\text{H}_2\text{O}$ [hexacobalt(II) bis(carbonate) octahydroxide monohydrate], though the hydroxide anions and water molecules are disordered on the same atomic sites, *i.e.* O2, O3 and O4 (Fig. 1). A thermogravimetric analysis (TGA) is fully consistent with this new formula (Fig. 2). The total weight loss after decomposition into Co_3O_4 , CO_2 and H_2O in the presence of oxygen is 25.98%, which is close to the theoretical value of 26.06%. The results of the Rietveld refinements are shown in Fig. 3. Crystal data, data collection and structure refinement details are summarized in Table 1.

3. Results and discussion

The title compound has similarities with $\text{Co}_2(\text{OH})_2\text{CO}_3$ (Wang *et al.*, 2010a; González-López *et al.*, 2017), itself isomorphous with either rosacite [$\text{Cu}_{1.5}\text{Zn}_{0.5}\text{CO}_3(\text{OH})_2$; Perchiazzi, 2006] or malachite [$\text{Cu}_2(\text{OH})_2\text{CO}_3$; Zigan *et al.*, 1977]. They both have a short *c* axis, *i.e.* 3.12244 (15) and 3.188 (4) Å, respectively, characteristic of infinite chains of edge-sharing [CoO_6] octahedra. There are two independent Co atom sites, one of them, Co2, being half occupied. Therefore, a projection of the structure along the short *c* axis (Fig. 1) shows tunnels surrounded by rings of nine [CoO_6] octahedra, three of which are empty. In each pseudo-ring, the partial-occupancy Co atoms are disordered in such a way as to avoid the unacceptably short Co2···Co2 contact (2.29 Å) that would occur if the Co atoms were linked through a face of the CoO_6 octahedron, the disorder being then the consequence of the absence of correlation between adjacent pseudo-rings. A bond valence analysis (see Table 2 in the supporting information)

shows that the C1–O1 distance is too short, whereas the Co–O distances are a little too long, possibly due to neglecting the H atoms in the refinements. The water molecule would preferably be located at the O2 site. Fig. 4 shows a possible local random arrangement of the Co2 atoms, showing how the tunnels are larger in reality. **CCH** synthesized by our method has a nanoneedle morphology, with an average diameter of ~40 nm, and can be formed as an electrode material with excellent battery-type performance (Bhojane & Shirage, 2019), in which the tunnel structure very probably plays a significant role.

During the identification step, the unindexed JCPDS card 038-0547 (PDF, 2012), corresponding to the formula Co-

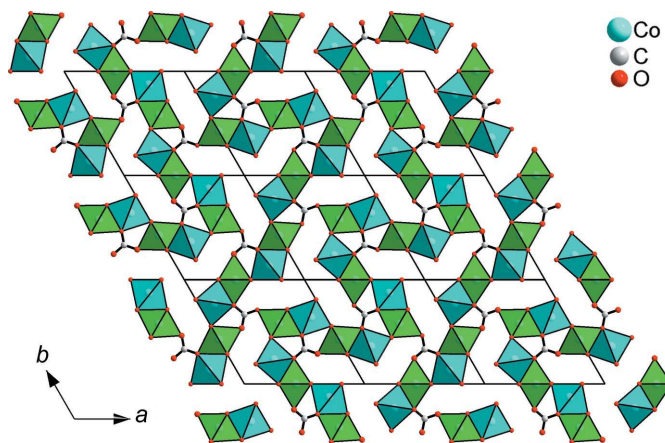


Figure 4

Respecting randomly the half occupancy of the Co2 atom site, the tunnels appear considerably more extended with a three-branched star section. But they have to accommodate ten H atoms per cell, two of them forming the unique water molecule in the $\text{Co}_6(\text{CO}_3)_2(\text{OH})_8\cdot\text{H}_2\text{O}$ formula ($Z = 1$), but they are difficult to locate since the site multiplicities of the O atoms are either 3 or 6.

$(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}\cdot 1.74\text{H}_2\text{O}$ (Lorenz & Kempe, 1984), was observed to have a powder pattern very similar to that of the title compound, so that it can be concluded that both are very probably isostructural. It should be noted that for the Cl/(OH)-based compound, the Co/(CO₃) ratio is close to 3, as expected now that **CCH** has been reformulated (it was originally 2). Thus, the Cl/(OH)-based compound was chronologically the first to adopt this new structure-type.

Most of the more than 200 papers based on the title compound have used and provide a false formula and a false indexing of the powder pattern (Wang *et al.*, 2010*b*; Xiong *et al.*, 2012; Zhu *et al.*, 2013; Li *et al.*, 2015); **CCH** is generally used as a precursor for preparing anode material in mesoporous Co₃O₄ for lithium-ion-battery applications. The pore size seems important in determining the final performance. The three-branched tunnel section in the **CCH** precursor may now explain why mesoporous Co₃O₄ is formed *via* direct thermal decomposition in laboratory air at temperatures in the range 573–673 K. The reaction is said to be topotactic; at least the **CCH** needle elongation direction which was given as [100] in the wrong orthorhombic cell has to be corrected to [001] of the hexagonal cell.

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supporting information

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Computing details

Program(s) used to solve structure: *McMaille* (Le Bail, 2004) and *ESPOIR* (Le Bail, 2001); program(s) used to refine structure: *FULLPROF* (Rodriguez-Carvajal, 1993); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Hexacobalt(II) bis(carbonate) octahydroxide monohydrate

Crystal data

Co₆(CO₃)₂(OH)₈·H₂O

M_r = 627.69

Hexagonal, *P*6̄2*m*

Hall symbol: P -6 -2

a = 10.3236 (4) Å

c = 3.12244 (15) Å

V = 288.20 (2) Å³

Z = 1

F(000) = 304

D_x = 3.617 Mg m⁻³

Synchrotron radiation, λ = 0.807700 Å

μ = 12.06 mm⁻¹

T = 293 K

Particle morphology: powder of nanoneedles
light pink

cylinder, 0.5 × 0.5 mm

Specimen preparation: Prepared at 293 K

Data collection

MAR345dif

diffractometer

Radiation source: synchrotron

Specimen mounting: quartz capillary

Data collection mode: transmission

Scan method: step

2θ_{min} = 3.883°, 2θ_{max} = 58.870°, 2θ_{step} = 0.020°

Refinement

R_p = 3.714

R_{wp} = 4.827

R_{exp} = 2.465

R_{Bragg} = 3.948

2805 data points

50 parameters

0 restraints

H-atom parameters not refined

(Δ/σ)_{max} < 0.001

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}	Occ. (<1)
Co1	0.42427 (12)	0.00000	0.00000	0.0180 (4)*	
Co2	0.36174 (19)	0.2336 (2)	0.50000	0.0328 (7)*	0.500
O1	0.5360 (4)	0.2464 (4)	0.00000	0.0278 (9)*	

O2	0.1908 (5)	0.1908 (5)	0.00000	0.0278 (9)*
O3	0.5545 (6)	0.00000	0.50000	0.0278 (9)*
O4	0.2852 (7)	0.00000	0.50000	0.0278 (9)*
C1	0.66667	0.33333	0.00000	0.0278 (9)*

Geometric parameters (\AA , $^\circ$)

Co1—O1	2.206 (4)	Co2—O1 ⁱⁱⁱ	2.335 (4)
Co1—O3	2.060 (4)	Co2—O2	2.229 (4)
Co1—O4	2.121 (5)	Co2—O4	2.130 (2)
Co1—O3 ⁱ	2.060 (4)	Co2—O2 ⁱⁱⁱ	2.229 (4)
Co1—O4 ⁱ	2.121 (5)	Co2—O3 ^{iv}	1.908 (6)
Co1—O1 ⁱⁱ	2.206 (4)	O1—C1	1.189 (4)
Co2—O1	2.335 (4)		
O1—Co1—O3	92.01 (8)	Co2—O2—Co2 ⁱ	88.9 (2)
O1—Co1—O4	87.92 (8)	Co2—O2—Co2 ^v	120.7 (2)
O1—Co1—O3 ⁱ	92.01 (8)	Co2—O2—Co2 ^{vi}	61.87 (10)
O1—Co1—O4 ⁱ	87.92 (8)	Co2 ⁱ —O2—Co2 ^v	61.87 (10)
O1—Co1—O1 ⁱⁱ	173.9 (2)	Co2 ⁱ —O2—Co2 ^{vi}	120.7 (2)
O3—Co1—O4	83.34 (19)	Co2 ^v —O2—Co2 ^{vi}	88.94 (17)
O3—Co1—O3 ⁱ	98.53 (19)	Co1—O3—Co1 ⁱⁱⁱ	98.5 (3)
O3—Co1—O4 ⁱ	178.1 (2)	Co1—O3—Co2 ^{vii}	121.46 (6)
O1 ⁱⁱ —Co1—O3	92.01 (11)	Co1—O3—Co2 ^{viii}	121.46 (6)
O3 ⁱ —Co1—O4	178.1 (2)	Co1 ⁱⁱⁱ —O3—Co2 ^{vii}	121.46 (6)
O4—Co1—O4 ⁱ	94.8 (2)	Co1 ⁱⁱⁱ —O3—Co2 ^{viii}	121.46 (6)
O1 ⁱⁱ —Co1—O4	87.92 (12)	Co2 ^{vii} —O3—Co2 ^{viii}	73.8 (3)
O3 ⁱ —Co1—O4 ⁱ	83.34 (19)	Co1—O4—Co2	97.59 (11)
O1 ⁱⁱ —Co1—O3 ⁱ	92.01 (11)	Co1—O4—Co1 ⁱⁱⁱ	94.8 (3)
O1 ⁱⁱ —Co1—O4 ⁱ	87.92 (12)	Co1—O4—Co2 ^{ix}	97.60 (12)
O2—Co2—O4	88.10 (19)	Co1 ⁱⁱⁱ —O4—Co2	97.59 (11)
O2—Co2—O2 ⁱⁱⁱ	88.94 (17)	Co2—O4—Co2 ^{ix}	157.5 (4)
O2—Co2—O3 ^{iv}	95.0 (2)	Co1 ⁱⁱⁱ —O4—Co2 ^{ix}	97.60 (12)
O2 ⁱⁱⁱ —Co2—O4	88.10 (19)	O1—C1—O1 ^x	120.0 (4)
O3 ^{iv} —Co2—O4	175.6 (3)	O1—C1—O1 ^{vii}	120.0 (3)
O2 ⁱⁱⁱ —Co2—O3 ^{iv}	95.0 (2)	O1 ^x —C1—O1 ^{vii}	120.0 (4)
Co1—O1—C1	127.7 (3)		
O3—Co1—O1—C1	49.31 (13)	O3—Co1—O4—Co2	98.33 (17)
O4—Co1—O1—C1	132.56 (15)	O2—Co2—O4—Co1	87.6 (2)
O1—Co1—O4—Co2	6.07 (19)		

Symmetry codes: (i) $x, y, z-1$; (ii) $x-y, -y, -z$; (iii) $x, y, z+1$; (iv) $-x+y+1, -x+1, -z+1$; (v) $y, x, z-1$; (vi) y, x, z ; (vii) $-y+1, x-y, z$; (viii) $-x+1, -x+y, z$; (ix) $x-y, -y, -z+1$; (x) $-x+y+1, -x+1, -z$.

Valence bond analysis according to the empirical expression from Brown and Altermatt [Brown, I. D. and Altermatt, D. (1985). *Acta Cryst. B41*, 244–247], using parameters for solids from Brese and O'Keeffe [Brese, N. E. and O'Keeffe, M. (1991). *Acta Cryst. B47*, 192–197]. The valence deficit observed for atoms O2, O3 and O4 is expected to be compensated by hydrogen bonding and the water molecule would be preferentially located on the O2 site.

	O1	O2	O3	O4	Σ	$\Sigma(\text{expected})$
Co1	0.245×2		0.363×2	0.308×2	1.83	2
Co2	0.173×2	0.230×2	0.547	0.301	1.65	2
C1	1.721×3	$\times 2$			5.16	4
Σ	2.14	0.46	1.23	0.92		
$\Sigma(\text{expected})$	2	2	2	2		