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

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

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The successful attempt to solve the crystal structure of Co(CO$_3$)$_{0.5}$(OH)·0.11H$_2$O (denoted CCH), based on synchrotron powder diffraction data, leads to a drastic revision of the chemical formula to Co$_6$(CO$_3$)$_2$(OH)$_8$·H$_2$O [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 [CoO$_6$] 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 Co$_3$O$_4$ have, as a result, to be reconsidered.

1. Introduction
Since 2010, more than 200 papers have cited Co(CO$_3$)$_{0.5}$(OH)·0.11H$_2$O (formula frequently included in the title), denoted for short CCH, as being a precursor of textured and mesoporous Co$_3$O$_4$ applied as the electrode material for supercapacitors and lithium-ion batteries (see, for example, Wang et al., 2010b; 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(NO$_3$)$_2$·6H$_2$O, 0.5 M urea and 10 mM NH$_4$Cl 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
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 ‘Co(CO3)0.5(OH)/C10.11H2O’ (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 (Rodriguez-Carvajal, 1993; Rietveld, 1969) in Le Bail fitting mode (Le Bail, 2005). Structure solution 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 CO3 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 \( P62m \) 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...
located. Therefore, the chemical composition, defined in the 48-0083 JCPDS card to be Co(CO₃)₀.₅(OH)/C₈.¹₁H₂O, has to be changed to Co₆(CO₃)₂(OH)₈/H₂O. Cobalt cations being Co²⁺ would mean eight OH⁻ anions and one water molecule, leading to the alternative formula Co₆(CO₃)₂(OH)₈/H₂O [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 Co₃O₄, CO₂ and H₂O 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 Co₂(OH)₂CO₃ (Wang et al., 2010a; González-López et al., 2017), itself isomorphous with either rosacite [Cu₁.₅Zn₀.₅CO₃(OH)₂; Perchiazzi, 2006] or malachite [Cu₂(OH)₉CO₃; 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 [CoO₆] 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 [CoO₆] 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 CoO₆ 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-
(CO\textsubscript{3})\textsubscript{0.35}Cl\textsubscript{0.20}(OH)\textsubscript{1.10}0.35Cl\textsubscript{0.20}(OH)\textsubscript{1.10}1.74H\textsubscript{2}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/(CO\textsubscript{3}) 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., 2010b; 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 Co\textsubscript{3}O\textsubscript{4} 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 Co\textsubscript{3}O\textsubscript{4} 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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References

Bhojane, P. & Shirage, P. M. (2019). In preparation.
Brandenburg, K. (1999). DIAMOND. Crystal Impact GbR, Bonn, Germany.
González-López, J., Cockcroft, J. K., Fernández-González, Á., Jimenez, A. & Grau-Crespo, R. (2017). Acta Cryst. B73, 868–873.
Le Bail, A. (2001). Mater. Sci. Forum, 378, 65–70.
Le Bail, A. (2004). Powder Diffr. 19, 249–254.
Le Bail, A. (2005). Powder Diffr. 20, 316–326.
Li, Y., Li, J., Zhang, S., Wang, N. & Zhou, Z. (2015). Int. J. Electrochem. Sci. 10, 8005–8016.
Lorenz, M. & Kempe, G. (1984). J. Therm. Anal. 29, 581–588.
PDF (2012). PDF4+ database. International Centre for Diffraction Data, Newtown Square, PA.
Perchiazzi, N. (2006). Z. Kristallogr. Suppl. 23, 505–510.
Porta, P., Dragone, R., Fierro, G., Inversi, M., Lo Jacono, M. & Moretti, G. (1992). J. Chem. Soc. Faraday Trans. 88, 311–319.
Rietveld, H. M. (1969). J. Appl. Cryst. 2, 65–71.
Rodriguez-Carvajal, J. (1993). Physica B, 192, 55–69.
Spek, A. L. (2009). Acta Cryst. D65, 148–155.
Wang, S., Lü, G. & Tang, W. (2010a). Powder Diffr. 25, S7–S10.
Wang, Y., Xia, H., Lu, L. & Lin, J. Y. (2010b). ACS Nano, 4, 1425–1432.
Westrip, S. P. (2010). J. Appl. Cryst. 43, 920–925.
Xiong, S. L., Chen, J. S., Lou, X. W. & Zeng, H. C. (2012). Adv. Funct. Mater. 22, 861–871.
Zhu, L., Wen, Z., Mei, W., Li, Y. & Ye, Z. (2013). J. Phys. Chem. C, 117, 20465–20473.
Zigan, F., Joswig, W., Schuster, H. D. & Mason, S. A. (1977). Z. Kristallogr. 145, 412–426.
A quarter of a century after its synthesis and with >200 papers based on its use, `Co(CO\textsubscript{3})\textsubscript{0.5}(OH)\cdot0.11\textsubscript{H_2}O' proves to be Co\textsubscript{6}(CO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{8}\cdot\textsubscript{H_2}O from synchrotron powder diffraction data

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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: publCIF (Westrip, 2010).

Hexacobalt(II) bis(carbonate) octahydroxide monohydrate

Crystal data

\[ \text{Co}_6(\text{CO}_3)_2(\text{OH})_8\cdot\text{H}_2\text{O} \]

\[ M_r = 627.69 \]

Hexagonal, \( \text{P}\text{6}\text{2}m \)

Hall symbol: \( \text{P} -6 -2 \)

\[ a = 10.3236 \ (4) \ \text{Å} \]

\[ c = 3.12244 \ (15) \ \text{Å} \]

\[ V = 288.20 \ (2) \ \text{Å}^3 \]

\[ Z = 1 \]

\[ F(000) = 304 \]

Data collection

MAR345dif

diffractometer

Radiation source: synchrotron

Specimen mounting: quartz capillary

Data collection mode: transmission

Scan method: step

\[ 2\theta_{\text{min}} = 3.883^\circ, 2\theta_{\text{max}} = 58.870^\circ, 2\theta_{\text{step}} = 0.020^\circ \]

Refinement

\[ R_p = 3.714 \]

\[ R_{wp} = 4.827 \]

\[ R_{exp} = 2.465 \]

\[ R_{\text{Bragg}} = 3.948 \]

50 parameters

0 restraints

H-atom parameters not refined

\( (\Delta/\sigma)_{\text{max}} < 0.001 \)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\textsuperscript{2})

|        | \( x \)    | \( y \)    | \( z \)    | \( U_{iso}{/*U_{eq}} \) | 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)* |           |
Geometric parameters (Å, °)

| Bond/Distance | Value 1 | Value 2 | Value 3 | Value 4 |
|---------------|---------|---------|---------|---------|
| Co1—O1        | 2.206 (4) | Co2—O1ii | 2.335 (4) |
| Co1—O3        | 2.060 (4) | Co2—O2   | 2.229 (4) |
| Co1—O4        | 2.121 (5) | Co2—O4   | 2.130 (2) |
| Co1—O3i       | 2.060 (4) | Co2—O2i  | 2.229 (4) |
| Co1—O4i       | 2.121 (5) | Co2—O3ii | 1.908 (6) |
| Co1—O1ii      | 2.206 (4) | O1—C1    | 1.189 (4) |
| Co2—O1        | 2.335 (4) | O1—Co1   | 92.01 (8)  |
| Co1—O1—O3     | 92.01 (8) | Co2—O2—Co2i | 88.9 (2) |
| Co1—O1—O4     | 87.92 (8) | Co2—O2—Co2iv | 120.7 (2) |
| Co1—O3i—O4i   | 92.01 (8) | Co2—O2—Co2iv | 120.7 (2) |
| Co1—O4i—O1ii  | 87.92 (8) | Co2—O2—Co2iv | 120.7 (2) |
| Co1—O1—O3i    | 98.53 (19) | Co1—O3—Co1iii | 98.5 (3) |
| Co1—O3i—O4i   | 98.53 (19) | Co1—O3—Co1vii | 98.5 (3) |
| Co1—O3i—O4i   | 178.1 (2)  | Co1—O3—Co1vi | 94.8 (3) |
| O1—Co1—O3     | 92.01 (11) | Co1—O4—Co1iii | 94.8 (3) |
| O1—Co1—O4     | 178.1 (2)  | Co1—O4—Co1v   | 97.60 (12) |
| O4—Co1—O4i    | 94.8 (2)   | Co1—O4—Co1vi | 97.60 (12) |
| Co1—O3i—O4i   | 87.92 (12) | Co1—O4—Co1vit | 157.5 (4) |
| O2—Co2—O1     | 89.10 (19) | Co1—O4—Co1vix | 97.60 (12) |
| O2—Co2—O3     | 88.94 (17) | Co1—O4—Co1vxi | 97.60 (12) |
| O2—Co2—O3iv   | 95.0 (2)   | O1—C1—O1v   | 120.0 (4) |
| Co1—O1—C1     | 127.7 (3)  | O1—C1—O1vii | 120.0 (4) |

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   | Σ(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   |             |             |             | 5.16| 4           |
| Σ    | 2.14        | 0.46        | 1.23        | 0.92        |     |             |
| Σ(expected) | 2 | 2 | 2 | 2 |     |             |