

catena-Poly[[cobalt(II)- μ -aqua- μ -propanoato- κ^2 O:O'- μ -propanoato- κ^2 O:O] monohydrate]

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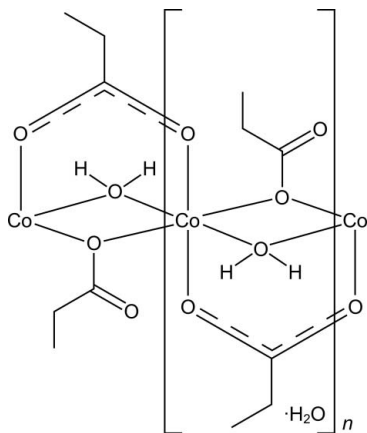
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Key indicators: single-crystal X-ray study; $T = 170$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.067; data-to-parameter ratio = 21.2.

The title compound, $\{[\text{Co}(\text{C}_2\text{H}_5\text{COO})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, was synthesized by the reaction of cobalt(II) carbonate hydrate with aqueous propionic acid. The structure consists of polymeric infinite linear chains with composition $[\text{Co}(\text{C}_2\text{H}_5\text{COO})_{4/2}(\text{H}_2\text{O})_{2/2}]_\infty$ running along [010]. The chains are formed by Co^{2+} ions linked with bridging propionate groups and water molecules, with a $\text{Co}\cdots\text{Co}$ distance along the chains of 3.2587 (9) Å. The Co^{2+} ion is six-coordinated in a strongly distorted octahedral geometry. The chains are connected to each other by a network of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds involving solvent water molecules.

Related literature

For the related cobalt(II) acetate dihydrate, see: Jiao *et al.* (2000). For the structure of a hydrated cobalt(II) acetate which has been isolated in similar conditions, see: Sobolev *et al.* (2003). For properties and applications of cobalt carboxylates, see: Eremenko *et al.* (2009); Gates (1992); Parshall & Ittel (1992); Partenheimer (1995).



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Experimental

Crystal data

$[\text{Co}(\text{C}_2\text{H}_5\text{O}_2)_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$
 $M_r = 241.10$
 Monoclinic, $C2/c$
 $a = 13.997$ (4) Å
 $b = 6.4987$ (18) Å
 $c = 21.440$ (6) Å
 $\beta = 103.216$ (5)°
 $V = 1898.6$ (9) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 1.81$ mm⁻¹
 $T = 170$ K
 $0.5 \times 0.3 \times 0.2$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
 $T_{\min} = 0.276$, $T_{\max} = 0.332$
 11986 measured reflections
 2762 independent reflections
 2542 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.067$
 $S = 1.09$
 2762 reflections
 130 parameters
 5 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.57$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H11}\cdots\text{O6}^i$	0.92 (3)	1.72 (3)	2.620 (2)	163 (3)
$\text{O1}-\text{H12}\cdots\text{O5}$	0.89 (3)	1.78 (3)	2.660 (2)	171 (3)
$\text{O5}-\text{H51}\cdots\text{O4}^{ii}$	0.92 (3)	1.90 (3)	2.794 (2)	163 (3)
$\text{O5}-\text{H52}\cdots\text{O2}^{iii}$	0.87 (3)	1.91 (3)	2.773 (2)	174 (3)

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, y, -z + \frac{1}{2}$; (iii) $-x + 1, y + 1, -z + \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2358).

References

- Brandenburg, K. (2008). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2007). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker, (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Eremenko, I. L., Sidorov, A. A. & Kiskin, M. A. (2009). *Magnetic Nanoparticles*, edited by S. P. Gubin, pp. 349–391. Weinheim: Wiley-VCH.
 Gates, B. C. (1992). *Catalytic Chemistry*. New York: Wiley-Interscience.
 Jiao, X.-D., Guzei, I. A. & Espenson, J. H. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 173–174.
 Parshall, G. W. & Ittel, S. D. (1992). *Homogenous Catalysis*. New York: Wiley-Interscience.
 Partenheimer, W. (1995). *Catal. Today*, **23**, 69–158.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sobolev, A. N., Miminoshvili, E. B., Miminoshvili, K. E. & Sakvarelidze, T. N. (2003). *Acta Cryst.* **E59**, m836–m837.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2010). E66, m1498 [https://doi.org/10.1107/S1600536810043540]

catena-Poly[[cobalt(II)- μ -aqua- μ -propanoato- κ^2 O:O'- μ -propanoato- κ^2 O:O] monohydrate]

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S1. Comment

Cobalt carboxylates are of great importance because of their application in homogeneous oxidation catalysis (Gates, 1992; Parshall & Ittel, 1992; Partenheimer, 1995), and their interesting magnetic properties (Eremenko *et al.*, 2009). Carboxylate ligands coordinated to transition metal ions can adopt different binding modes and form a great number of various cage complexes and a variety of different one-dimensional, two-dimensional and three-dimensional structures.

The title compound, $[\text{Co}(\text{C}_2\text{H}_5\text{COO})_2(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (**I**), actually named as cobalt(II) propionate dihydrate, is attracting our attention as the starting substance for the synthesis of mixed-valence cobalt carboxylates. This salt was synthesized and its crystal structure is reported herein.

The crystal structure of (**I**) contains one symmetrically independent Co^{2+} cation coordinated to four O atoms of four bridging propionates and two O atoms of bridging water molecules in a strongly distorted octahedral coordination (Fig. 1). The *cis*-angles about the Co atom range from 77.35 (4) to 109.40 (5)°, the Co—O bond length ranges from 2.0406 (12) to 2.2460 (12) Å; this is in agreement with the angles and the distances in isostructural cobalt(II) acetate dihydrate (Jiao *et al.*, 2000). The structure of (**I**) consists of polymeric infinite linear chains with composition ${}_x[\text{Co}(\text{C}_2\text{H}_5\text{COO})_{4/2}(\text{H}_2\text{O})_{2/2}]$ running along [010]. The Co...Co separation is 3.2587 (9) Å. The bridging carboxylate groups adopt two coordination modes, monodentate and *syn-syn* bidentate. The bidentate carboxylate group has C—O bonds of equal length, 1.267 (2) Å, whereas monodentate carboxylate group has different C—O bond lengths, 1.235 (2) and 1.305 (2) Å. The chains are connected to each other by a network of hydrogen bonds to solvate water molecules (Fig. 2).

It is rather interesting that the use of acetic acid instead of propionic acid in the synthesis of (**I**) result in the formation of monomeric cobalt(II) acetate tetrahydrate (Sobolev *et al.*, 2003), and the polymeric cobalt(II) acetate dihydrate is formed by recrystallization of cobalt(II) acetate tetrahydrate from acetic acid (Jiao *et al.*, 2000).

S2. Experimental

To a solution of propionic acid (7.4 g, 100 mmol) in water (15 ml), an excess of fresh cobalt(II) carbonate hydrate, $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$, (8.0 g, approximately 60 mmol) was added. The reaction mixture was stirred for 8 h at room temperature, followed by filtrating the unreacted $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ out. The filtrate was allowed to stand at room temperature for slow evaporation. The red single crystals of (**I**) suitable for X-ray diffraction studies were obtained after several days. Yield 85%.

S3. Refinement

For a single-crystal X-ray diffraction experiment, a red transparent crystal of (**I**) was mounted on the Bruker Smart *APEX* II diffractometer. The experiment was performed at 170 K. The structure was solved by the direct method and refined using *SHELXL-97* program (Sheldrick, 2008). The positions of hydrogen atoms of water molecules were localized from

the differential Fourier synthesis and H atoms of the CH₂ and CH₃ groups were calculated by the algorithm incorporated in the *SHELXL* program complex. Hydrogen atoms kept fixed with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

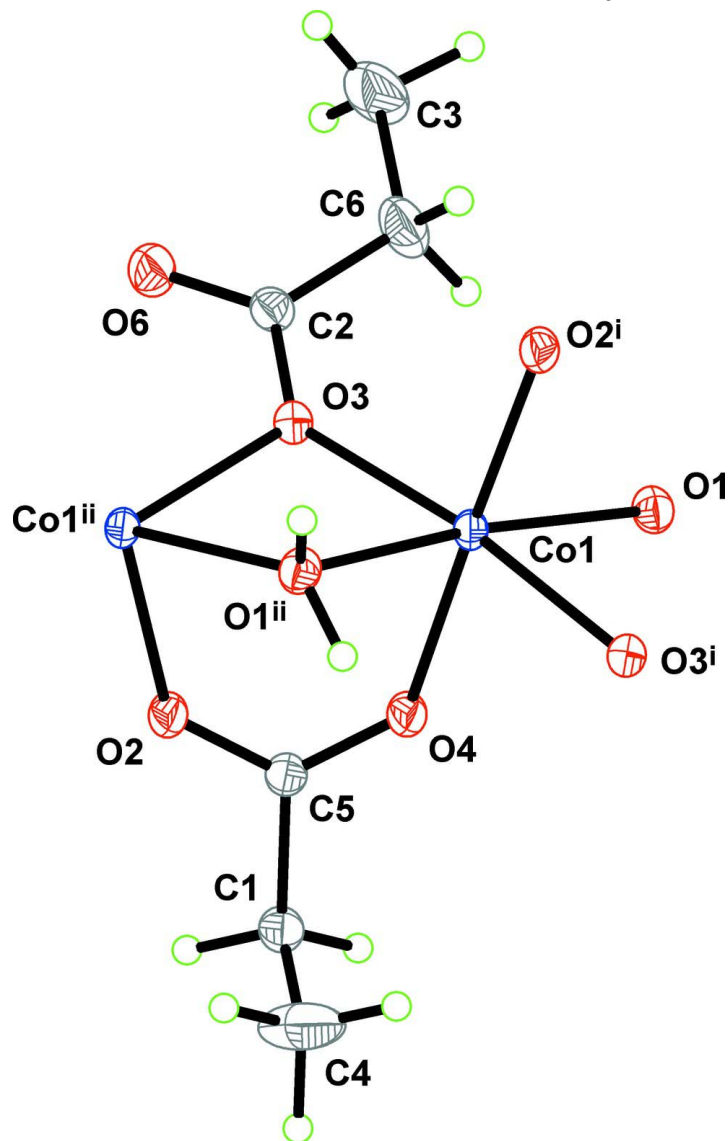


Figure 1

The coordinated mode and linkage of the complex (I). Displacement ellipsoids of non-H atoms are drawn at the 40% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. Symmetry codes: i = $-x + 1/2, y + 1/2, -z + 1/2$; ii = $-x + 1/2, y - 1/2, -z + 1/2$.]

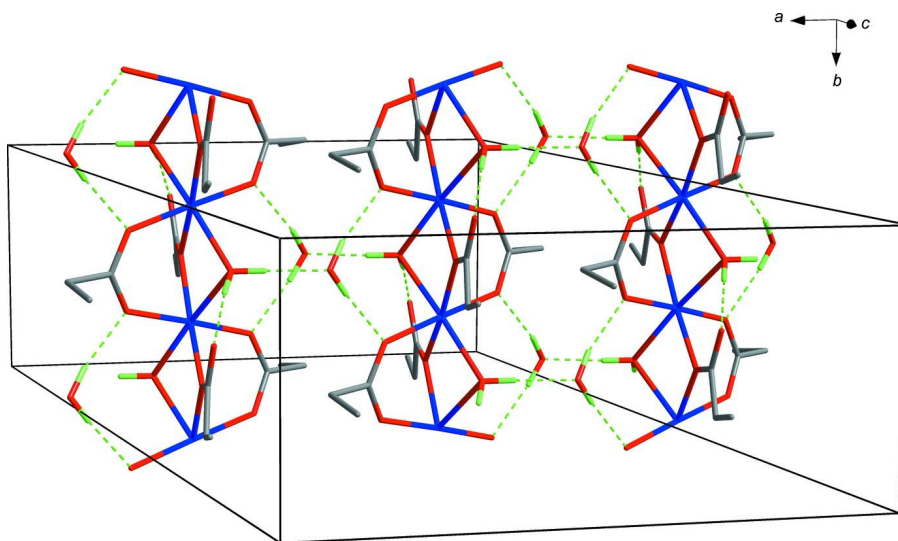


Figure 2

Sticks representation of the crystal structure of (I) showing hydrogen bonds as green dashed lines. Only the H atoms involved in hydrogen bonds are shown. Co atoms are blue, O atoms are red, C atoms are grey, and selected H atoms are green colored.]

catena-Poly[[cobalt(II)- μ -aqua- μ -propanoato- κ^2 O:O'- μ -propanoato- κ^2 O:O] monohydrate]

Crystal data

[Co(C₃H₅O₂)₂(H₂O)]·H₂O

$M_r = 241.10$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 13.997(4) \text{ \AA}$

$b = 6.4987(18) \text{ \AA}$

$c = 21.440(6) \text{ \AA}$

$\beta = 103.216(5)^\circ$

$V = 1898.6(9) \text{ \AA}^3$

$Z = 8$

$F(000) = 1000$

$D_x = 1.687 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 7703 reflections

$\theta = 2.9\text{--}35.9^\circ$

$\mu = 1.81 \text{ mm}^{-1}$

$T = 170 \text{ K}$

Prism, red

$0.5 \times 0.3 \times 0.2 \text{ mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.276$, $T_{\max} = 0.332$

11986 measured reflections

2762 independent reflections

2542 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -19 \rightarrow 19$

$k = -9 \rightarrow 9$

$l = -30 \rightarrow 30$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.067$

$S = 1.09$

2762 reflections

130 parameters

5 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 1.4667P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.248706 (13)	0.18331 (3)	0.244111 (9)	0.01830 (7)
O1	0.29927 (8)	0.44228 (16)	0.19444 (5)	0.0231 (2)
H11	0.267 (2)	0.511 (5)	0.1580 (14)	0.080*
H12	0.362 (2)	0.441 (5)	0.1918 (16)	0.080*
O2	0.39246 (8)	-0.23440 (17)	0.29662 (6)	0.0262 (2)
O3	0.23831 (8)	-0.08151 (15)	0.18689 (5)	0.0217 (2)
O4	0.39309 (8)	0.10838 (17)	0.28586 (5)	0.0246 (2)
O5	0.47910 (10)	0.4367 (2)	0.17307 (8)	0.0391 (3)
H51	0.516 (2)	0.328 (5)	0.1935 (15)	0.080*
H52	0.517 (2)	0.543 (4)	0.1846 (16)	0.080*
O6	0.21765 (10)	-0.29849 (19)	0.10436 (6)	0.0338 (3)
C1	0.53359 (12)	-0.0526 (3)	0.35261 (9)	0.0304 (3)
H1A	0.5732	0.0598	0.3390	0.046*
H1B	0.5683	-0.1860	0.3505	0.046*
C2	0.21658 (11)	-0.1222 (2)	0.12565 (7)	0.0229 (3)
C3	0.1606 (2)	0.0073 (4)	0.01094 (10)	0.0580 (7)
H3A	0.1450	0.1368	-0.0146	0.087*
H3B	0.1013	-0.0834	0.0029	0.087*
H3C	0.2157	-0.0660	-0.0021	0.087*
C4	0.52401 (19)	-0.0140 (5)	0.42103 (11)	0.0600 (7)
H4A	0.5908	-0.0101	0.4503	0.090*
H4B	0.4847	-0.1272	0.4346	0.090*
H4C	0.4902	0.1206	0.4231	0.090*
C5	0.43274 (11)	-0.0596 (2)	0.30805 (7)	0.0208 (3)
C6	0.19027 (18)	0.0594 (3)	0.08116 (9)	0.0418 (5)
H6A	0.1351	0.1358	0.0932	0.063*
H6B	0.2480	0.1544	0.0881	0.063*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01681 (10)	0.01335 (10)	0.02365 (11)	0.00019 (7)	0.00237 (7)	0.00019 (7)
O1	0.0216 (5)	0.0199 (5)	0.0281 (5)	0.0003 (4)	0.0061 (4)	0.0025 (4)
O2	0.0192 (5)	0.0173 (5)	0.0387 (6)	-0.0008 (4)	-0.0006 (4)	0.0004 (4)
O3	0.0247 (5)	0.0170 (5)	0.0221 (5)	0.0004 (4)	0.0026 (4)	0.0003 (4)
O4	0.0185 (5)	0.0181 (5)	0.0347 (6)	0.0001 (4)	0.0010 (4)	0.0004 (4)
O5	0.0241 (6)	0.0228 (6)	0.0687 (10)	0.0001 (5)	0.0068 (6)	0.0011 (6)
O6	0.0486 (8)	0.0254 (6)	0.0255 (5)	0.0056 (5)	0.0044 (5)	-0.0032 (4)
C1	0.0188 (7)	0.0231 (8)	0.0443 (9)	0.0001 (6)	-0.0034 (6)	0.0012 (6)
C2	0.0225 (7)	0.0225 (7)	0.0234 (6)	0.0027 (6)	0.0043 (5)	0.0012 (5)
C3	0.089 (2)	0.0507 (13)	0.0271 (9)	0.0158 (13)	-0.0012 (10)	0.0075 (9)
C4	0.0477 (13)	0.0883 (19)	0.0351 (10)	-0.0161 (13)	-0.0093 (9)	0.0042 (12)
C5	0.0170 (6)	0.0199 (7)	0.0253 (6)	0.0002 (5)	0.0044 (5)	-0.0005 (5)
C6	0.0667 (14)	0.0300 (9)	0.0270 (8)	0.0139 (9)	0.0069 (8)	0.0065 (7)

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

Co1—O2 ⁱ	2.0406 (12)	C1—C5	1.514 (2)
Co1—O4	2.0726 (12)	C1—C4	1.524 (3)
Co1—O3	2.0991 (11)	C1—H1A	1.0000
Co1—O3 ⁱ	2.1058 (11)	C1—H1B	1.0000
Co1—O1	2.1936 (12)	C2—C6	1.509 (2)
Co1—O1 ⁱⁱ	2.2460 (12)	C3—C6	1.506 (3)
O1—H11	0.92 (3)	C3—H3A	1.0000
O1—H12	0.89 (3)	C3—H3B	1.0000
O2—C5	1.2669 (18)	C3—H3C	1.0000
O3—C2	1.3053 (18)	C4—H4A	1.0000
O4—C5	1.2670 (18)	C4—H4B	1.0000
O5—H51	0.92 (3)	C4—H4C	1.0000
O5—H52	0.87 (3)	C6—H6A	1.0000
O6—C2	1.2346 (19)	C6—H6B	1.0000
O2 ⁱ —Co1—O4	178.40 (4)	C4—C1—H1A	109.7
O2 ⁱ —Co1—O3	91.94 (5)	C5—C1—H1B	109.7
O4—Co1—O3	89.44 (4)	C4—C1—H1B	109.7
O2 ⁱ —Co1—O3 ⁱ	91.72 (5)	H1A—C1—H1B	108.2
O4—Co1—O3 ⁱ	87.03 (4)	O6—C2—O3	122.70 (14)
O3—Co1—O3 ⁱ	171.46 (4)	O6—C2—C6	120.92 (14)
O2 ⁱ —Co1—O1	88.83 (5)	O3—C2—C6	116.38 (14)
O4—Co1—O1	89.94 (5)	C6—C3—H3A	109.5
O3—Co1—O1	109.40 (5)	C6—C3—H3B	109.5
O3 ⁱ —Co1—O1	78.38 (5)	H3A—C3—H3B	109.5
O2 ⁱ —Co1—O1 ⁱⁱ	92.50 (5)	C6—C3—H3C	109.5
O4—Co1—O1 ⁱⁱ	88.60 (5)	H3A—C3—H3C	109.5
O3—Co1—O1 ⁱⁱ	77.35 (4)	H3B—C3—H3C	109.5
O3 ⁱ —Co1—O1 ⁱⁱ	94.79 (5)	C1—C4—H4A	109.5

O1—Co1—O1 ⁱⁱ	173.08 (3)	C1—C4—H4B	109.5
Co1—O1—Co1 ⁱ	94.44 (5)	H4A—C4—H4B	109.5
Co1—O1—H11	129 (2)	C1—C4—H4C	109.5
Co1 ⁱ —O1—H11	90 (2)	H4A—C4—H4C	109.5
Co1—O1—H12	117 (2)	H4B—C4—H4C	109.5
Co1 ⁱ —O1—H12	118 (2)	O2—C5—O4	124.23 (14)
H11—O1—H12	104 (3)	O2—C5—C1	117.31 (13)
C5—O2—Co1 ⁱⁱ	131.47 (10)	O4—C5—C1	118.44 (13)
C2—O3—Co1	136.31 (10)	C3—C6—C2	115.31 (17)
C2—O3—Co1 ⁱⁱ	121.50 (10)	C3—C6—H6A	108.4
Co1—O3—Co1 ⁱⁱ	101.60 (5)	C2—C6—H6A	108.4
C5—O4—Co1	131.66 (10)	C3—C6—H6B	108.4
H51—O5—H52	104 (3)	C2—C6—H6B	108.4
C5—C1—C4	109.75 (16)	H6A—C6—H6B	107.5
C5—C1—H1A	109.7		

Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $-x+1/2, y-1/2, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H11 \cdots O6 ⁱⁱⁱ	0.92 (3)	1.72 (3)	2.620 (2)	163 (3)
O1—H12 \cdots O5	0.89 (3)	1.78 (3)	2.660 (2)	171 (3)
O5—H51 \cdots O4 ^{iv}	0.92 (3)	1.90 (3)	2.794 (2)	163 (3)
O5—H52 \cdots O2 ^v	0.87 (3)	1.91 (3)	2.773 (2)	174 (3)

Symmetry codes: (iii) $x, y+1, z$; (iv) $-x+1, y, -z+1/2$; (v) $-x+1, y+1, -z+1/2$.