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catena-Poly[[diaquacobalt(II)]-bis(μ -4-fluorobenzoato- κ^2 O:O')]

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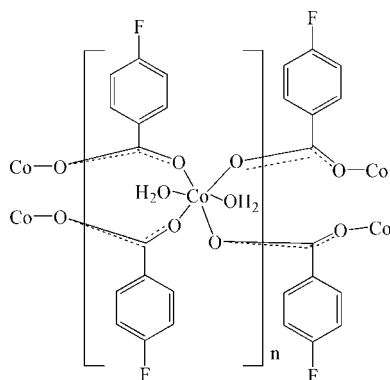
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 Key indicators: single-crystal X-ray study; $T = 290$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.032; wR factor = 0.087; data-to-parameter ratio = 15.2.

The hydrothermal reaction of CoCO_3 and 4-fluorobenzoic acid afforded the title Co^{II} complex, $[\text{Co}(\text{C}_7\text{H}_4\text{FO}_2)_2(\text{H}_2\text{O})_2]_n$. The Co^{II} atom is located on an inversion center and is coordinated by six O atoms from two water molecules and four μ_2 -carboxylate groups of 4-fluorobenzoate anions, forming a distorted CoO_6 octahedron, with $\text{Co}-\text{O}$ bond lengths in the range 2.071 (2)–2.130 (2) Å. All adjacent $\text{O}-\text{Co}-\text{O}$ angles are in the range 84.78 (6)–95.22 (6)° and opposite angles are 180.0°. Each μ -carboxylate group of the 4-fluorobenzoate anions bridges two symmetry-related Co^{II} atoms. Hydrogen-bonding interactions of the coordinated water molecules further connect the cobalt–carboxylate units, forming layers perpendicular to the a axis. The cobalt–oxygen layers are encased in a sandwich-like fashion by layers of π -stacked 4-fluorobenzoate anions. Within these layers the benzene rings of the 4-fluorobenzoate anions are π -stacked, with centroid–centroid distances of 3.432 (4) Å.

Related literature

For other complexes of the 2(or 4)-fluorobenzoato ligand, see: Zhang (2006c); Zhang *et al.* (2005a,b). For related structures, see: Zhang (2004, 2005, 2006a,b,c); Zhang *et al.* (2008); Majumder *et al.* (2006); Shi *et al.* (1996).



Experimental

Crystal data

 $[\text{Co}(\text{C}_7\text{H}_4\text{FO}_2)_2(\text{H}_2\text{O})_2]$
 $M_r = 373.17$
 Monoclinic, $P2_1/c$
 $a = 14.866$ (3) Å
 $b = 6.6043$ (13) Å
 $c = 7.3081$ (15) Å
 $\beta = 100.94$ (3)°

 $V = 704.5$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.27$ mm⁻¹
 $T = 290$ K
 $0.54 \times 0.35 \times 0.10$ mm

Data collection

 Rigaku R-Axis RAPID
 diffractometer
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.590$, $T_{\text{max}} = 0.879$

 6437 measured reflections
 1616 independent reflections
 1432 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.087$
 $S = 1.15$
 1616 reflections

 106 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{O2}-\text{H2B}\cdots\text{O3}^{\text{i}}$ | 0.85 | 2.00 | 2.833 (2) | 167 |
| $\text{O2}-\text{H2A}\cdots\text{O3}^{\text{ii}}$ | 0.85 | 2.11 | 2.835 (2) | 143 |
| $\text{O2}-\text{H2A}\cdots\text{O1}^{\text{iii}}$ | 0.85 | 2.42 | 3.115 (1) | 140 |

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2189).

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supporting information

Acta Cryst. (2009). E65, m587–m588 [doi:10.1107/S1600536809014913]

catena-Poly[[diaquacobalt(II)]-bis(μ -4-fluorobenzoato- κ^2 O:O')]**Fu-Fu Zhou and Bi-Song Zhang****S1. Comment**

Cobalt(II) ions can form, among others, mononuclear and one-dimensional network complexes (Majumder *et al.*, 2006). In this context we have studied and reported the crystal structures of complexes with halobenzoate ligands, X—C₆H₄COO⁻, where X is F, Cl, Br or I, (Zhang, 2004, 2005, 2006*a,b,c*; Zhang *et al.*, 2005, 2008). In this report we would like to report the synthesis and crystal structure of the title complex, ² ∞ [Co(H₂O)₂(FC₆H₄COO)_{4/2}]. Within the title compound, each Co^{II} atom is located on a crystallographic inversion center and is coordinated by six O atoms from two water molecules and four μ_2 -carboxyl groups of 4-fluorobenzoic acid anions, to form a distorted CoO₆ octahedron, with Co—O bond lengths in the range of 2.071 (2) to 2.130 (2) Å. All adjacent O—Co—O bond angles are in the range of 84.78 (6)–95.22 (6)° and opposite angles are 180.0 (1)°.

Each μ_2 -carboxyl group of the 4-fluorobenzoic anions bridges two symmetry related cobalt atoms, Co(1) and Co(1)^{vi} (vi: $-x + 1, -y, -z + 1$). Hydrogen bonding interactions of the coordinated water molecules further connect the cobalt-carboxylate units with each other to form layers perpendicular to the *a* axis (Fig.2). The O—H \cdots O bond lengths are in the range of 2.83 (2) to 3.12 (1) Å, the O—H \cdots O bond angles are in the range of 139.7 (1) —167.0 (1)°, Table 2. The cobalt-oxygen layers are encased in a sandwich like fashion by layers of π -stacked 4-fluorobenzoate anions. Within these layers the benzene rings of the 4-fluorobenzoate anions are π stacked with centroid to centroidⁱⁱⁱ (iii = $x, 0.5-y, -0.5+z$) distances of 3.432 (4)Å.

S2. Experimental

CoCO₃ (0.132 g, 1.110 mmol), 4-fluorobenzoic acid (0.085 g, 0.607 mmol) and 15 ml CH₃OH/H₂O (1:2, *v/v*) were mixed and stirred for *ca* 5.0 h, and the resulting suspension was heated in a 23 ml Teflon-lined stainless steel autoclave at 433 K for 6 days. After the autoclave cooled to room temperature, the solid was filtered off. The resulting purple filtrate was allowed to stand at room temperature and slow evaporation over three months gave red block crystals suitable for X-ray analysis. Yield: 76%.

S3. Refinement

C-bound H atoms were placed in calculated positions, with C—H = 0.93Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and were refined using the riding-model approximation. The H atoms of the water molecule were located in a difference Fourier map and refined with an O—H distance restraint of 0.85 (1) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

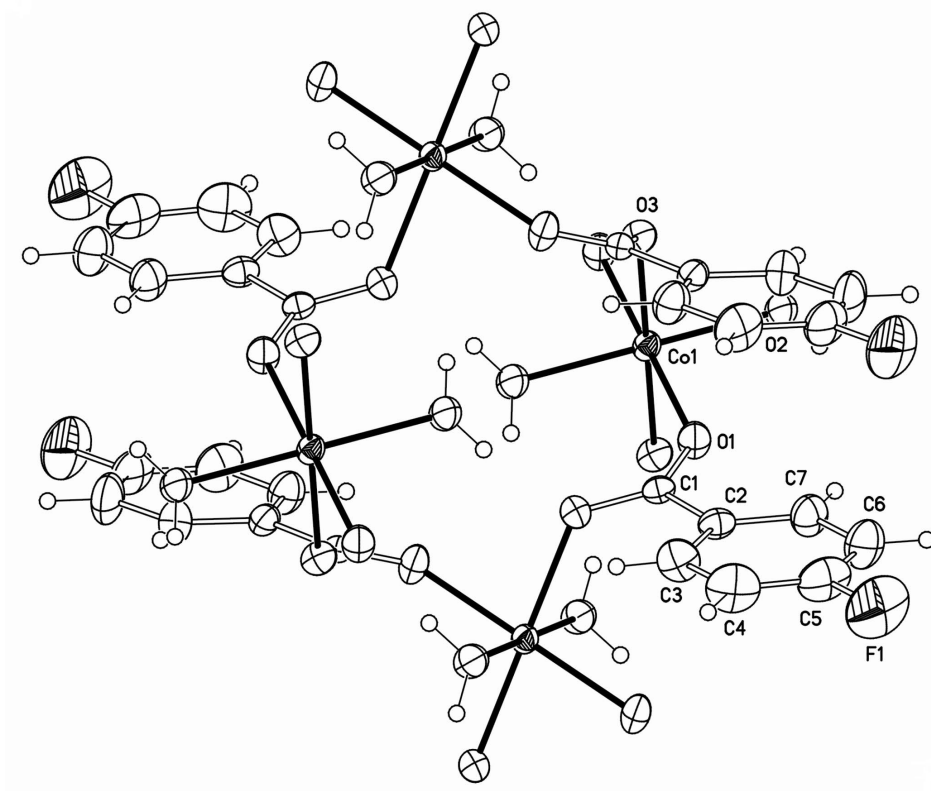


Figure 1

The structure unit of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

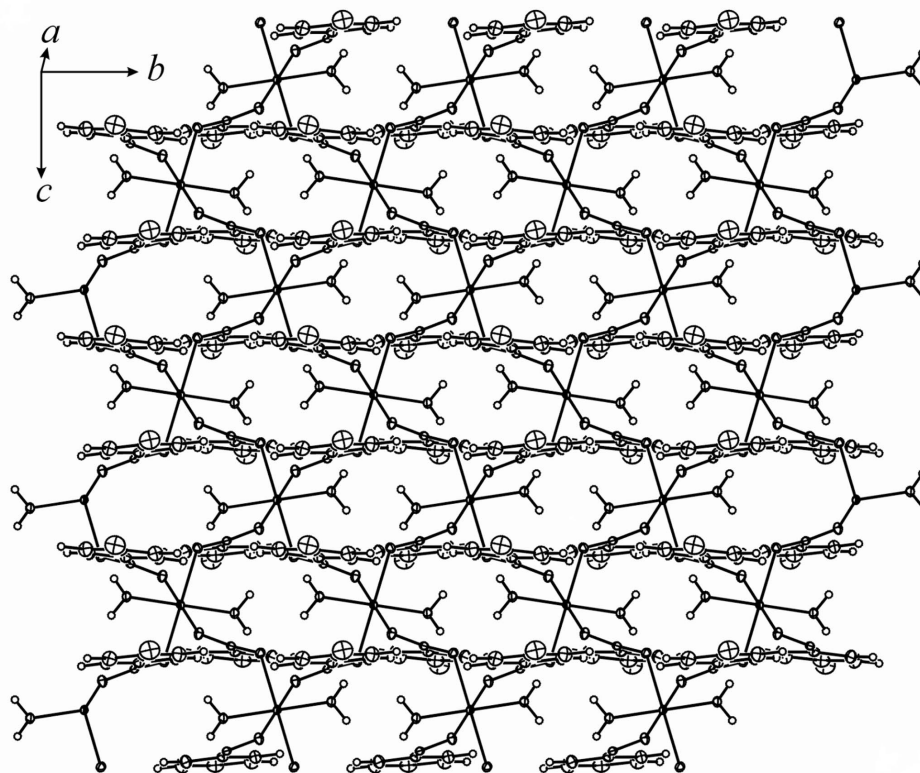


Figure 2

View of the title complex along the [100] direction showing the two-dimensional layering.

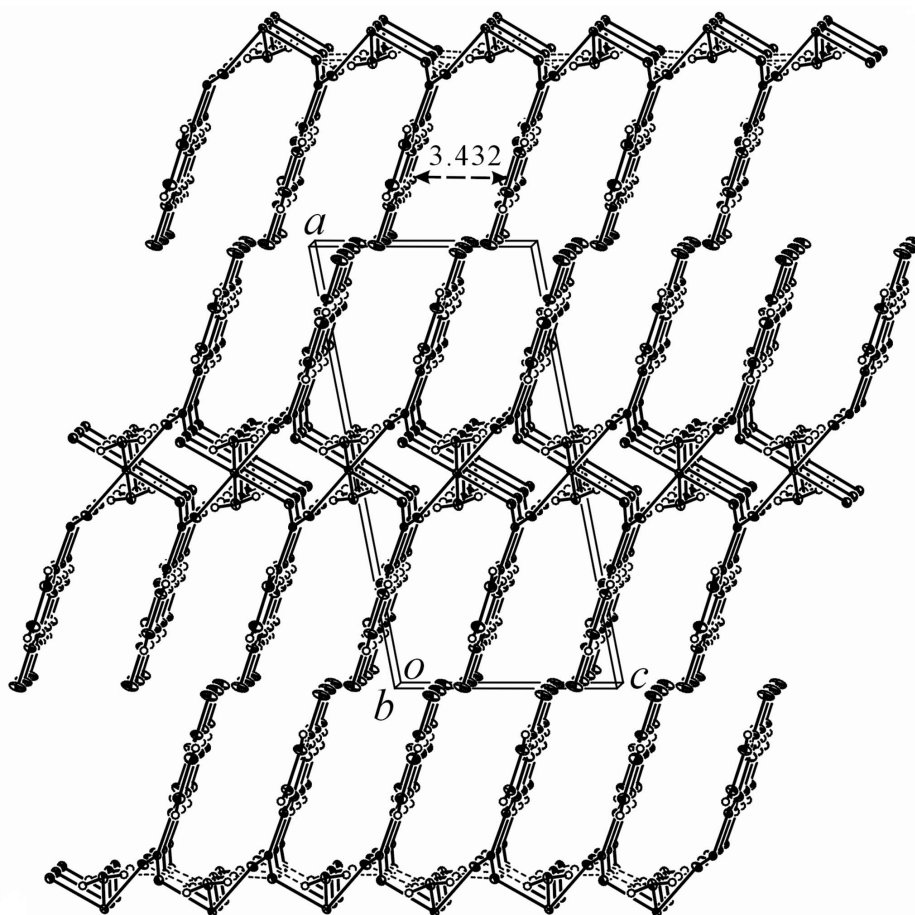


Figure 3

A packing diagram of the title complex, viewed along the *b* axis. π - π Stacking interactions are indicated as dashed double arrows.

catena-Poly[[diaquacobalt(II)]-bis(μ -4-fluorobenzoato- κ^2 O:O')]

Crystal data

[Co(C₇H₄FO₂)₂(H₂O)₂]

$M_r = 373.17$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 14.866$ (3) Å

$b = 6.6043$ (13) Å

$c = 7.3081$ (15) Å

$\beta = 100.94$ (3)°

$V = 704.5$ (3) Å³

$Z = 2$

$F(000) = 378$

$D_x = 1.759$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5552 reflections

$\theta = 3.4$ – 27.5 °

$\mu = 1.27$ mm⁻¹

$T = 290$ K

Block, red

$0.54 \times 0.35 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.590$, $T_{\max} = 0.879$

6437 measured reflections

1616 independent reflections
 1432 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.4^\circ$

$h = -19 \rightarrow 19$
 $k = -7 \rightarrow 8$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.087$
 $S = 1.15$
 1616 reflections
 106 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.6464P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{\AA}^{-3}$

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 $F^2 > \sigma(F^2)$ 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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|------------|----------------------------------|
| Co1 | 0.5000 | 0.0000 | 0.5000 | 0.01947 (14) |
| O1 | 0.60194 (11) | 0.0944 (2) | 0.7171 (2) | 0.0278 (3) |
| O2 | 0.56707 (11) | -0.2799 (2) | 0.5136 (2) | 0.0285 (3) |
| H2B | 0.5729 | -0.3586 | 0.6071 | 0.043* |
| H2A | 0.5482 | -0.3444 | 0.4130 | 0.043* |
| O3 | 0.57083 (10) | 0.0875 (2) | 0.2851 (2) | 0.0260 (3) |
| F1 | 0.98672 (12) | 0.3394 (4) | 1.1685 (3) | 0.0776 (7) |
| C1 | 0.62472 (14) | 0.2606 (3) | 0.7934 (3) | 0.0202 (4) |
| C2 | 0.72091 (14) | 0.2833 (4) | 0.8984 (3) | 0.0255 (4) |
| C3 | 0.75685 (19) | 0.4727 (4) | 0.9486 (4) | 0.0378 (6) |
| H3 | 0.7203 | 0.5873 | 0.9217 | 0.045* |
| C4 | 0.8473 (2) | 0.4922 (5) | 1.0391 (5) | 0.0504 (8) |
| H4 | 0.8725 | 0.6190 | 1.0720 | 0.060* |
| C5 | 0.89849 (18) | 0.3206 (5) | 1.0786 (4) | 0.0487 (7) |
| C6 | 0.86542 (18) | 0.1311 (5) | 1.0332 (4) | 0.0476 (7) |
| H6 | 0.9021 | 0.0173 | 1.0633 | 0.057* |
| C7 | 0.77507 (17) | 0.1134 (4) | 0.9404 (4) | 0.0358 (5) |
| H7 | 0.7509 | -0.0139 | 0.9063 | 0.043* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|--------------|--------------|
| Co1 | 0.0219 (2) | 0.0161 (2) | 0.0191 (2) | -0.00099 (14) | 0.00055 (14) | 0.00070 (13) |
| O1 | 0.0262 (8) | 0.0231 (8) | 0.0306 (8) | -0.0007 (6) | -0.0034 (6) | -0.0042 (6) |
| O2 | 0.0390 (9) | 0.0198 (8) | 0.0254 (8) | 0.0022 (6) | 0.0027 (6) | 0.0007 (6) |
| O3 | 0.0287 (8) | 0.0240 (8) | 0.0249 (7) | -0.0049 (6) | 0.0041 (6) | 0.0012 (6) |
| F1 | 0.0302 (9) | 0.1146 (19) | 0.0775 (14) | -0.0175 (11) | -0.0163 (9) | -0.0037 (13) |
| C1 | 0.0217 (9) | 0.0223 (10) | 0.0169 (9) | -0.0031 (8) | 0.0045 (7) | 0.0005 (7) |
| C2 | 0.0237 (10) | 0.0312 (12) | 0.0212 (10) | -0.0044 (9) | 0.0026 (8) | -0.0023 (8) |
| C3 | 0.0354 (13) | 0.0341 (14) | 0.0425 (15) | -0.0079 (10) | 0.0036 (11) | -0.0060 (11) |
| C4 | 0.0389 (15) | 0.055 (2) | 0.0544 (18) | -0.0201 (14) | 0.0005 (13) | -0.0115 (13) |
| C5 | 0.0241 (12) | 0.079 (2) | 0.0398 (15) | -0.0120 (13) | -0.0031 (10) | -0.0034 (14) |
| C6 | 0.0291 (13) | 0.0597 (19) | 0.0491 (16) | 0.0079 (12) | -0.0049 (11) | 0.0031 (14) |
| C7 | 0.0300 (12) | 0.0362 (14) | 0.0378 (13) | 0.0008 (10) | -0.0024 (9) | -0.0020 (10) |

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

| | | | |
|--------------------------------------|-------------|--------------------------|-------------|
| Co1—O1 ⁱ | 2.0712 (16) | C1—C2 | 1.497 (3) |
| Co1—O1 | 2.0712 (16) | C2—C7 | 1.381 (3) |
| Co1—O2 ⁱ | 2.0938 (16) | C2—C3 | 1.382 (3) |
| Co1—O2 | 2.0938 (16) | C3—C4 | 1.387 (4) |
| Co1—O3 | 2.1301 (15) | C3—H3 | 0.9300 |
| Co1—O3 ⁱ | 2.1301 (15) | C4—C5 | 1.365 (5) |
| O1—C1 | 1.248 (3) | C4—H4 | 0.9300 |
| O2—H2B | 0.8500 | C5—C6 | 1.362 (5) |
| O2—H2A | 0.8500 | C6—C7 | 1.390 (4) |
| O3—C1 ⁱⁱ | 1.278 (3) | C6—H6 | 0.9300 |
| F1—C5 | 1.357 (3) | C7—H7 | 0.9300 |
| C1—O3 ⁱⁱⁱ | 1.278 (3) | | |
| O1 ⁱ —Co1—O1 | 180.00 (10) | O1—C1—C2 | 117.95 (19) |
| O1 ⁱ —Co1—O2 ⁱ | 87.54 (6) | O3 ⁱⁱⁱ —C1—C2 | 118.37 (18) |
| O1—Co1—O2 ⁱ | 92.46 (6) | C7—C2—C3 | 119.8 (2) |
| O1 ⁱ —Co1—O2 | 92.46 (6) | C7—C2—C1 | 119.5 (2) |
| O1—Co1—O2 | 87.54 (6) | C3—C2—C1 | 120.7 (2) |
| O2 ⁱ —Co1—O2 | 180.00 (9) | C2—C3—C4 | 120.1 (3) |
| O1 ⁱ —Co1—O3 | 84.78 (6) | C2—C3—H3 | 120.0 |
| O1—Co1—O3 | 95.22 (6) | C4—C3—H3 | 120.0 |
| O2 ⁱ —Co1—O3 | 91.33 (6) | C5—C4—C3 | 118.4 (3) |
| O2—Co1—O3 | 88.67 (6) | C5—C4—H4 | 120.8 |
| O1 ⁱ —Co1—O3 ⁱ | 95.22 (6) | C3—C4—H4 | 120.8 |
| O1—Co1—O3 ⁱ | 84.78 (6) | F1—C5—C6 | 118.3 (3) |
| O2 ⁱ —Co1—O3 ⁱ | 88.67 (6) | F1—C5—C4 | 118.4 (3) |
| O2—Co1—O3 ⁱ | 91.33 (6) | C6—C5—C4 | 123.4 (2) |
| O3—Co1—O3 ⁱ | 180.00 (6) | C5—C6—C7 | 117.8 (3) |
| C1—O1—Co1 | 134.73 (14) | C5—C6—H6 | 121.1 |
| Co1—O2—H2B | 123.6 | C7—C6—H6 | 121.1 |

| | | | |
|--------------------------|-------------|----------|-----------|
| Co1—O2—H2A | 109.0 | C2—C7—C6 | 120.6 (3) |
| H2B—O2—H2A | 110.8 | C2—C7—H7 | 119.7 |
| C1 ⁱⁱ —O3—Co1 | 124.82 (13) | C6—C7—H7 | 119.7 |
| O1—C1—O3 ⁱⁱⁱ | 123.68 (19) | | |

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

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|---------------------------|------------|--------------|--------------|----------------|
| O2—H2B...O3 ^{iv} | 0.85 | 2.00 | 2.833 (2) | 167 |
| O2—H2A...O3 ^v | 0.85 | 2.11 | 2.835 (2) | 143 |
| O2—H2A...O1 ^{vi} | 0.85 | 2.42 | 3.115 (1) | 140 |

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