

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Hexaaquacobalt(II) 3,3'-dicarboxy-biphenyl-4,4'-dicarboxylate

 Yu-Hua Zhang,^{a*} Jin-Mei Han^b and Zong-Ze Li^b

^aSchool of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, Jiangsu 221008, People's Republic of China, and ^bSchool of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan University, Kunming 650091, People's Republic of China

Correspondence e-mail: amudulin@gmail.com

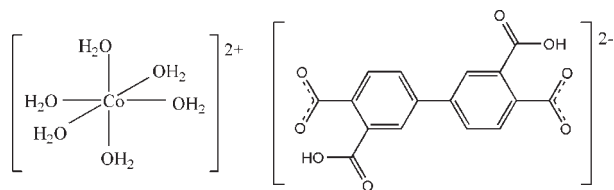
Received 24 June 2010; accepted 19 July 2010

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.048; wR factor = 0.169; data-to-parameter ratio = 10.9.

In the crystal structure of the title compound, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ($\text{C}_{16}\text{H}_8\text{O}_8$), both the cation and anion are centrosymmetric. The Co cation displays a CoO_6 octahedral geometry formed by six water molecules. In the anion, the two carboxyl groups are oriented at dihedral angles of 4.8 (5) and 10.4 (7)° with respect to the benzene ring. Very strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the protonated and deprotonated carboxylate groups occur. Neighbouring cations and anions are connected through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds into a three-dimensional supramolecular structure.

Related literature

For related metal complexes with the biphenyl-3,3',4,4'-tetracarboxylate ligand, see: Sun *et al.* (2009); Wang *et al.* (2005, 2006). For the structures containing the 4,4'-dicarboxy-biphenyl-3,3'-dicarboxylate ligand, see: Kang *et al.* (2009a,b); Zhu *et al.* (2008).



Experimental

Crystal data

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{C}_{16}\text{H}_8\text{O}_8)$
 $M_r = 495.25$
 Triclinic, $P\bar{1}$
 $a = 6.5197$ (14) Å
 $b = 7.9514$ (17) Å
 $c = 9.664$ (2) Å

$\alpha = 76.339$ (2)°
 $\beta = 87.656$ (2)°
 $\gamma = 86.221$ (2)°
 $V = 485.57$ (18) Å³
 $Z = 1$
 Mo $K\alpha$ radiation

$\mu = 0.96$ mm⁻¹
 $T = 293$ K

0.23 × 0.19 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.804$, $T_{\max} = 0.895$

2871 measured reflections
 1590 independent reflections
 1305 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.169$
 $S = 1.00$
 1590 reflections
 146 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.43$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O5	2.054 (3)	Co1—O7	2.082 (3)
Co1—O6	2.027 (3)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O4	0.85 (2)	1.55 (2)	2.391 (5)	173 (8)
O5—H5B \cdots O4 ⁱ	0.96	2.17	2.820 (5)	124
O5—H5C \cdots O2 ⁱⁱ	0.96	1.97	2.789 (4)	142
O6—H6A \cdots O3 ⁱⁱⁱ	0.96	1.84	2.676 (4)	144
O6—H6C \cdots O1 ⁱⁱ	0.96	1.79	2.708 (4)	159
O7—H7A \cdots O1 ^{iv}	0.96	1.83	2.749 (5)	159
O7—H7C \cdots O3	0.96	1.99	2.822 (5)	144

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2789).

References

- Bruker (2001). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Kang, J., Huang, C.-C., Jiang, Z.-Q., Huang, S. & Huang, S.-L. (2009a). *Acta Cryst.* E65, m452.
 Kang, J., Huang, C.-C., Zhai, L.-S., Qin, X.-H. & Liu, Z.-Q. (2009b). *Acta Cryst.* E65, m380–m381.
 Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.
 Sun, L.-X., Qi, Y., Che, Y.-X., Batten, S. R. & Zheng, J.-M. (2009). *Cryst. Growth Des.* 9, 2995–2998.
 Wang, X.-L., Cao, Q. & Wang, E.-B. (2005). *Eur. J. Inorg. Chem.* pp. 3418–3421.
 Wang, X.-L., Cao, Q. & Wang, E.-B. (2006). *Cryst. Growth Des.* 6, 439–433.
 Zhu, S., Zhang, H. & Shao, M. (2008). *Transition Met. Chem.* 33, 669–680.

supporting information

Acta Cryst. (2010). E66, m1007 [https://doi.org/10.1107/S1600536810028771]

Hexaaquacobalt(II) 3,3'-dicarboxybiphenyl-4,4'-dicarboxylate**Yu-Hua Zhang, Jin-Mei Han and Zong-Ze Li****S1. Comment**

Biphenyl-3,3',4,4'-tetracarboxylic acid have been used to construct high-dimensional supramolecular networks due to their versatile coordination modes and potential covalent or hydrogen bonding interactions with related parts in the assembly process (Sun *et al.* 2009; Wang *et al.* 2005) such as one-dimensional covalent zigzag chain coexist with one-dimensional hydrogen-bonded ladder (Wang *et al.* 2006). Here we reported a mononuclear complex, containing two ionic components of complex $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{16}\text{H}_{18}\text{O}_8)$ (I) in which the two parts are connected *via* O—H \cdots O hydrogen bonds forming a three-dimensional framework. The structure of the compound (I) consists of discrete ionic entities. A labeled diagram of the crystal $[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{16}\text{H}_{18}\text{O}_8)$ is shown in Fig. 1. In the cations, the metal atom is surrounded by six aqua ligands, exhibiting a slightly distorted octahedral stereochemistry. The *cis/trans* O—Co—O angles are nearly 90°. The average Co—O distance for compound (I) is 2.077 Å. The anion 3,3',4,4'-biphenyltetralate contain inversion center. The mean plane was calculated throughout the six atoms of the benzene ring. Because of symmetric reason, the two benzene rings of the biphenyl ligand are coplanar. The carboxylate groups are almost coplanar with the benzene ring with the largest deviation of -0.205 (6) Å for O4. As expected, there are considerable hydrogen bonds in the structure. The bond distances and angles are listed in Table 2. A three-dimensional structure was formed *via* three kinds of hydrogen bonds between the coordinated water molecules and carboxyl groups which also help to consolidate the crystal packing (Fig. 2).

S2. Experimental

A mixture of biphenyl-3,3',4,4'-tetracarboxylic acid (0.2 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.4 mmol) in 12 ml methanol/water (8:3) sealed in a 25 ml Teflon-lined stainless steel autoclave was kept at 393 K for three days. Single crystals suitable for the X-ray experiment were obtained.

S3. Refinement

The carboxyl H atom was located in a difference map and refined isotropically. The H atoms of aromatic ring and water molecules were generated geometrically and were included in the refinement in the riding model approximation with C—H = 0.93 Å, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ and O—H = 0.96 Å, $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$.

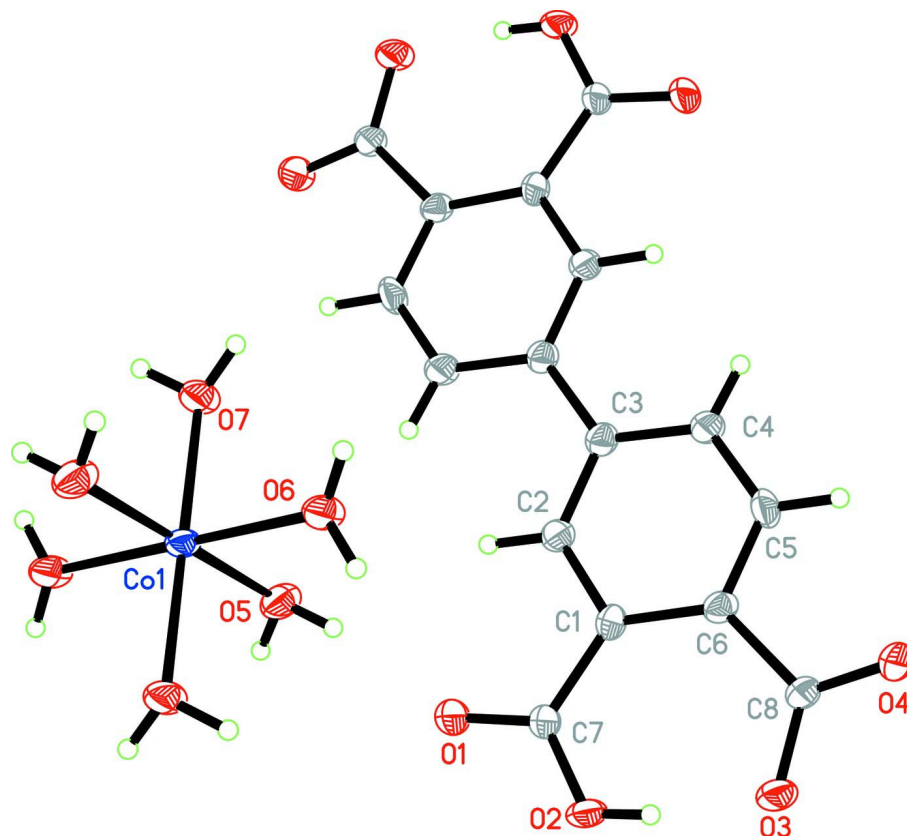


Figure 1

The molecular structure of the title complex with the atom-numbering diagram. Ellipsoids were drawn at the 30% probability level.

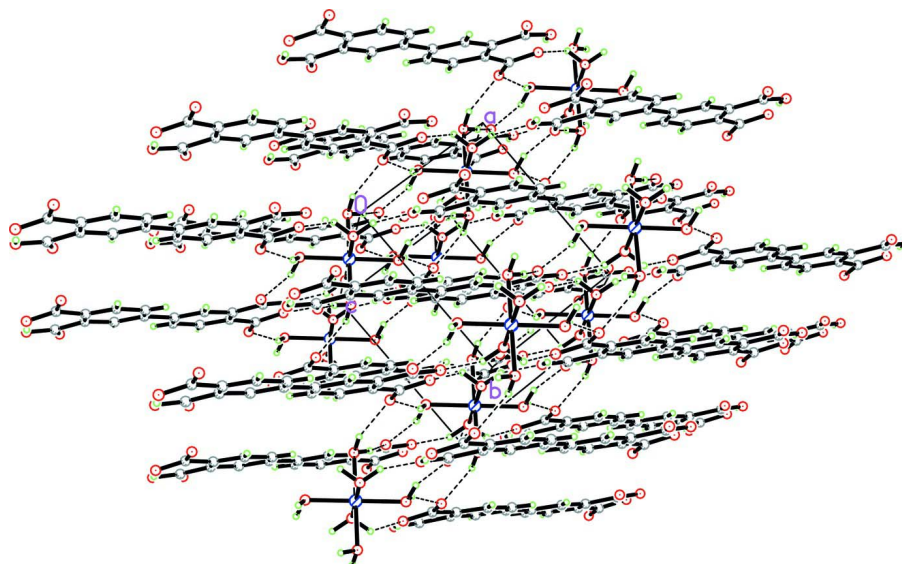


Figure 2

The packing diagram of (I). Hydrogen bonds are marked by dashed line.

Hexaaquacobalt(II) 3,3'-dicarboxybiphenyl-4,4'-dicarboxylate

Crystal data

[Co(H₂O)₆](C₁₆H₈O₈) $M_r = 495.25$ Triclinic, $P\bar{1}$ $a = 6.5197$ (14) Å $b = 7.9514$ (17) Å $c = 9.664$ (2) Å $\alpha = 76.339$ (2)° $\beta = 87.656$ (2)° $\gamma = 86.221$ (2)° $V = 485.57$ (18) Å³ $Z = 1$ $F(000) = 255$ $D_x = 1.694$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 774 reflections

 $\theta = 2.2$ – 25.0 ° $\mu = 0.96$ mm⁻¹ $T = 293$ K

Block, pink

 $0.23 \times 0.19 \times 0.12$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scansAbsorption correction: multi-scan
(*SADABS*; Bruker, 2001) $T_{\min} = 0.804$, $T_{\max} = 0.895$

2871 measured reflections

1590 independent reflections

1305 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.028$ $\theta_{\max} = 25.0$ °, $\theta_{\min} = 2.2$ ° $h = -7 \rightarrow 7$ $k = -9 \rightarrow 9$ $l = -11 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.169$ $S = 1.00$

1590 reflections

146 parameters

1 restraint

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.1263P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.47$ e Å⁻³ $\Delta\rho_{\min} = -0.43$ e Å⁻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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	1.0000	0.0000	0.5000	0.0281 (3)
O1	0.5091 (5)	0.1808 (4)	1.2457 (3)	0.0408 (8)
O2	0.3077 (5)	0.1278 (4)	1.0880 (4)	0.0396 (8)

O3	0.4682 (5)	0.2634 (5)	0.6417 (4)	0.0494 (10)
O4	0.2791 (5)	0.1755 (4)	0.8356 (3)	0.0417 (8)
O5	1.0135 (5)	-0.0174 (5)	0.2911 (3)	0.0434 (9)
H5B	0.9751	-0.1302	0.2858	0.065*
H5C	1.1512	-0.0002	0.2537	0.065*
O6	1.2248 (5)	0.1707 (5)	0.4594 (4)	0.0444 (9)
H6A	1.3079	0.1541	0.5419	0.067*
H6C	1.3089	0.1508	0.3803	0.067*
O7	0.7843 (5)	0.2081 (4)	0.4461 (4)	0.0441 (9)
H7A	0.6763	0.1760	0.3946	0.066*
H7C	0.7277	0.2372	0.5314	0.066*
C1	0.6112 (6)	0.2899 (5)	1.0027 (4)	0.0255 (9)
C2	0.7719 (6)	0.3637 (5)	1.0551 (5)	0.0257 (9)
H2B	0.7823	0.3463	1.1532	0.031*
C3	0.9157 (6)	0.4613 (5)	0.9679 (5)	0.0267 (9)
C4	0.8945 (7)	0.4888 (6)	0.8216 (5)	0.0336 (10)
H4B	0.9850	0.5580	0.7599	0.040*
C5	0.7413 (7)	0.4147 (6)	0.7674 (5)	0.0358 (11)
H5A	0.7335	0.4324	0.6691	0.043*
C6	0.5974 (6)	0.3144 (5)	0.8535 (5)	0.0279 (9)
C7	0.4682 (6)	0.1923 (5)	1.1202 (5)	0.0288 (10)
C8	0.4405 (7)	0.2462 (6)	0.7705 (5)	0.0311 (10)
H2	0.293 (12)	0.152 (9)	0.999 (2)	0.10 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0215 (5)	0.0511 (6)	0.0143 (5)	-0.0164 (3)	0.0002 (3)	-0.0092 (4)
O1	0.0359 (17)	0.070 (2)	0.0193 (19)	-0.0237 (16)	0.0020 (14)	-0.0103 (15)
O2	0.0344 (17)	0.062 (2)	0.025 (2)	-0.0271 (15)	0.0024 (15)	-0.0103 (16)
O3	0.046 (2)	0.087 (3)	0.024 (2)	-0.0326 (19)	0.0002 (16)	-0.0224 (17)
O4	0.0316 (17)	0.066 (2)	0.032 (2)	-0.0238 (15)	0.0005 (14)	-0.0133 (16)
O5	0.0368 (18)	0.077 (2)	0.0222 (18)	-0.0290 (16)	0.0048 (14)	-0.0167 (16)
O6	0.0373 (18)	0.074 (2)	0.028 (2)	-0.0310 (16)	0.0045 (15)	-0.0191 (16)
O7	0.0361 (18)	0.070 (2)	0.0301 (19)	-0.0101 (16)	-0.0049 (15)	-0.0162 (16)
C1	0.025 (2)	0.032 (2)	0.022 (2)	-0.0069 (16)	0.0007 (17)	-0.0092 (17)
C2	0.026 (2)	0.034 (2)	0.018 (2)	-0.0103 (17)	-0.0028 (17)	-0.0074 (17)
C3	0.024 (2)	0.033 (2)	0.024 (2)	-0.0054 (17)	-0.0038 (18)	-0.0064 (17)
C4	0.038 (2)	0.045 (2)	0.022 (2)	-0.023 (2)	-0.0027 (19)	-0.0090 (19)
C5	0.042 (3)	0.045 (3)	0.024 (3)	-0.019 (2)	-0.002 (2)	-0.0117 (19)
C6	0.024 (2)	0.034 (2)	0.029 (3)	-0.0078 (17)	-0.0020 (18)	-0.0103 (18)
C7	0.028 (2)	0.037 (2)	0.026 (3)	-0.0109 (18)	0.0014 (19)	-0.0126 (18)
C8	0.029 (2)	0.040 (2)	0.029 (3)	-0.0118 (19)	-0.0047 (19)	-0.0137 (19)

Geometric parameters (Å, °)

Co1—O5	2.054 (3)	O7—H7A	0.9600
Co1—O5 ⁱ	2.054 (3)	O7—H7C	0.9600

Co1—O6	2.027 (3)	C1—C2	1.401 (6)
Co1—O6 ⁱ	2.027 (3)	C1—C6	1.415 (6)
Co1—O7	2.082 (3)	C1—C7	1.534 (6)
Co1—O7 ⁱ	2.082 (3)	C2—C3	1.383 (6)
O1—C7	1.233 (5)	C2—H2B	0.9300
O2—C7	1.276 (5)	C3—C4	1.390 (6)
O2—H2	0.85 (2)	C3—C3 ⁱⁱ	1.516 (8)
O3—C8	1.226 (6)	C4—C5	1.374 (6)
O4—C8	1.295 (5)	C4—H4B	0.9300
O5—H5B	0.9600	C5—C6	1.389 (6)
O5—H5C	0.9601	C5—H5A	0.9300
O6—H6A	0.9600	C6—C8	1.526 (6)
O6—H6C	0.9600		
O6—Co1—O6 ⁱ	180.0	C2—C1—C6	118.3 (4)
O6—Co1—O5	90.40 (13)	C2—C1—C7	113.4 (4)
O6 ⁱ —Co1—O5	89.60 (13)	C6—C1—C7	128.3 (4)
O6—Co1—O5 ⁱ	89.60 (13)	C3—C2—C1	123.2 (4)
O6 ⁱ —Co1—O5 ⁱ	90.40 (13)	C3—C2—H2B	118.4
O5—Co1—O5 ⁱ	180.0	C1—C2—H2B	118.4
O6—Co1—O7	88.72 (14)	C2—C3—C4	117.5 (4)
O6 ⁱ —Co1—O7	91.28 (14)	C2—C3—C3 ⁱⁱ	120.3 (5)
O5—Co1—O7	89.16 (14)	C4—C3—C3 ⁱⁱ	122.2 (5)
O5 ⁱ —Co1—O7	90.84 (14)	C5—C4—C3	120.6 (4)
O6—Co1—O7 ⁱ	91.28 (14)	C5—C4—H4B	119.7
O6 ⁱ —Co1—O7 ⁱ	88.72 (14)	C3—C4—H4B	119.7
O5—Co1—O7 ⁱ	90.83 (14)	C4—C5—C6	122.6 (4)
O5 ⁱ —Co1—O7 ⁱ	89.17 (14)	C4—C5—H5A	118.7
O7—Co1—O7 ⁱ	180.000 (1)	C6—C5—H5A	118.7
C7—O2—H2	111 (5)	C5—C6—C1	117.8 (4)
Co1—O5—H5B	109.3	C5—C6—C8	113.7 (4)
Co1—O5—H5C	109.4	C1—C6—C8	128.5 (4)
H5B—O5—H5C	109.5	O1—C7—O2	120.9 (4)
Co1—O6—H6A	109.3	O1—C7—C1	118.8 (4)
Co1—O6—H6C	109.1	O2—C7—C1	120.3 (4)
H6A—O6—H6C	109.5	O3—C8—O4	121.2 (4)
Co1—O7—H7A	109.1	O3—C8—C6	118.9 (4)
Co1—O7—H7C	109.5	O4—C8—C6	119.9 (4)
H7A—O7—H7C	109.5		
C6—C1—C2—C3	0.9 (6)	C2—C1—C6—C8	179.1 (4)
C7—C1—C2—C3	-178.3 (4)	C7—C1—C6—C8	-1.9 (7)
C1—C2—C3—C4	1.4 (6)	C2—C1—C7—O1	-2.9 (6)
C1—C2—C3—C3 ⁱⁱ	179.4 (4)	C6—C1—C7—O1	178.0 (4)
C2—C3—C4—C5	-2.8 (7)	C2—C1—C7—O2	175.6 (4)
C3 ⁱⁱ —C3—C4—C5	179.2 (5)	C6—C1—C7—O2	-3.5 (7)
C3—C4—C5—C6	2.0 (7)	C5—C6—C8—O3	9.6 (6)
C4—C5—C6—C1	0.3 (7)	C1—C6—C8—O3	-171.2 (4)

C4—C5—C6—C8	179.6 (4)	C5—C6—C8—O4	-168.7 (4)
C2—C1—C6—C5	-1.8 (6)	C1—C6—C8—O4	10.4 (7)
C7—C1—C6—C5	177.3 (4)		

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

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

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H2...O4	0.85 (2)	1.55 (2)	2.391 (5)	173 (8)
O5—H5B...O4 ⁱⁱⁱ	0.96	2.17	2.820 (5)	124
O5—H5C...O2 ^{iv}	0.96	1.97	2.789 (4)	142
O6—H6A...O3 ^v	0.96	1.84	2.676 (4)	144
O6—H6C...O1 ^{iv}	0.96	1.79	2.708 (4)	159
O7—H7A...O1 ^{vi}	0.96	1.83	2.749 (5)	159
O7—H7C...O3	0.96	1.99	2.822 (5)	144

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