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A second monoclinic polymorph of caesium salicylate monohydrate

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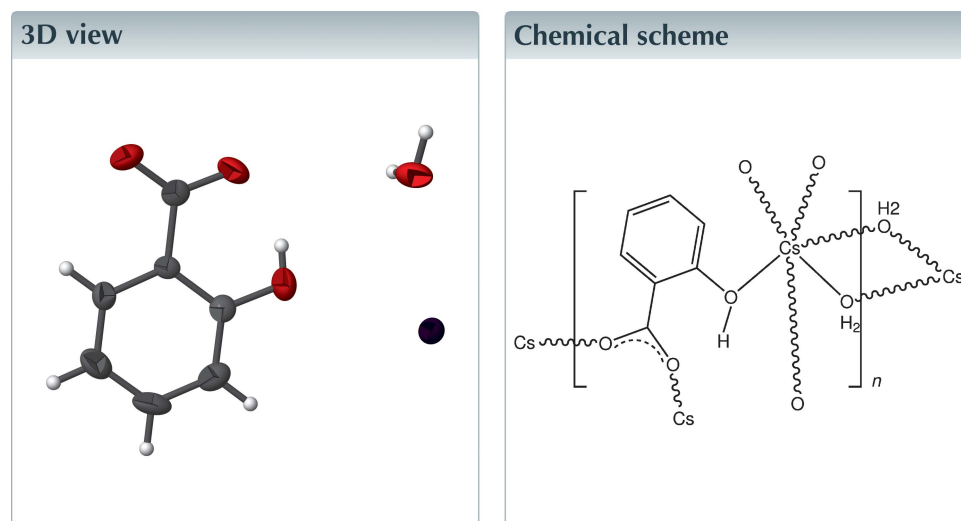
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Keywords: crystal structure; polymorphism; caesium salicylate.

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Structural data: full structural data are available from iucrdata.iucr.org

The structure of the title caesium salt with salicylic acid, poly[μ_2 -aqua- μ_4 -(salicylato- $\kappa^4 O^1:O^1:O^1:O^2$)caesium], $[\text{Cs}(\text{C}_7\text{H}_5\text{O}_3)(\text{H}_2\text{O})]_n$, represents a second monoclinic polymorph of this compound. The two-dimensional coordination polymeric structure is based on a centrosymmetric dinuclear bridged repeat unit with each irregular CsO_6 coordination polyhedron comprising a μ_2 -bridging water molecule and μ_4 -bridging O-atom donors, three from the carboxyl group and one from the phenolic group of the salicylate ligand. The Cs—O bond range is 3.023 (3)–3.368 (4) Å and the Cs···Cs separation within the dinuclear unit is 4.9265 (6) Å. The polymeric sheet structure lies parallel to (010) with the water molecule and the phenol group involved in intra-polymer O—H···O_{carboxyl} hydrogen-bonding interactions.



Structure description

In the title complex salt, $[\text{Cs}(\text{C}_7\text{H}_5\text{O}_3)(\text{H}_2\text{O})]_n$ (polymorph 2) (Fig. 1), although polymorphic with the Wiesbrock & Schmidbaur (2003a) crystal and forming a two-dimensional coordination polymeric structure, apart from the very obvious cell-parameter differences, particularly the disparate values of the unique b axis, the molecular structures are distinctly different. Polymorph 2 is based on a centrosymmetric dinuclear bridged repeat unit with each irregular CsO_6 coordination polyhedron comprising a μ_2 -bridging water molecule (O1W), and μ_4 -bridging O-atom donors, three from the carboxyl group and one from the phenolic group of the salicylate ligand. The Cs—O bond-length range is 3.023 (3)–3.368 (4) Å (Table 1) and the Cs···Csⁱⁱⁱ separation within the dinuclear unit is 4.9265 (6) Å. With polymorph 1, the Cs—O range in the CsO_7 coordination sphere is given as 3.071 (3)–3.584 (2) Å (although stated incorrectly as eight-coordinate), this would be reduced to CsO_6 with the last value in the stated range being considered too

Table 1
Selected bond lengths (Å).

Cs1—O12 ⁱ	3.023 (3)	Cs1—O11 ⁱⁱ	3.159 (4)
Cs1—O1W	3.108 (3)	Cs1—O12 ⁱⁱⁱ	3.244 (3)
Cs1—O2	3.130 (4)	Cs1—O1W ⁱⁱⁱ	3.368 (4)

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

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 O12	0.78 (6)	1.82 (6)	2.516 (5)	148 (8)
O1W—H11W \cdots O11 ^{iv}	0.89 (4)	2.00 (5)	2.867 (5)	165 (6)
O1W—H11W \cdots O12 ^v	0.89 (4)	2.57 (5)	3.268 (5)	136 (5)
O1W—H12W \cdots O11 ^v	0.89 (4)	2.04 (5)	2.848 (5)	151 (6)

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

long for a Cs—O bond (PLATON; Spek, 2009), with the sixth value being 3.341 (2) Å. The shortest Cs \cdots Cs separation in polymorph 1 is also very different [4.1391 (3) Å].

The polymeric sheet structure in the title complex lies parallel to (010) (Figs. 2 and 3) and in the crystal, intra-layer hydrogen-bonding interactions (Table 2) involving H-atom donors of the coordinating water molecule and carboxyl O-atom acceptors are present (Fig. 3). Also present are short Cs1 \cdots C interactions to four of the salicylate ring C atoms [C1^v 3.838 (4) Å; C4^v 3.825 (5) Å; C5^v 3.648 (5) Å; C6^v 3.658 (5) Å; for symmetry code (v), see Table 2].

With the salicylate anion, the carboxyl group is rotated slightly out of the benzene plane [torsion angle C2—C1—O11—C11 = -167.4 (4)°], comparing with -168.2 (3)° in polymorph 1 and 179.3 (1)° in the structure of the parent salicylic acid (Munshi & Guru Row, 2006). In all of the sali-

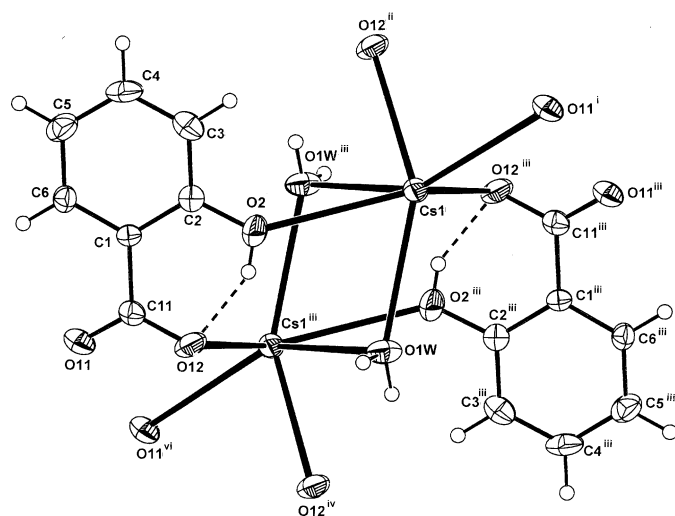


Figure 1
The molecular configuration and atom-numbering scheme for the centrosymmetric repeat unit in the title complex, with non-H atoms shown as 40% probability displacement ellipsoids. For symmetry codes, see Table 1. Hydrogen bonds are shown as dashed lines.

Table 3
Experimental details.

Crystal data	[Cs(C ₇ H ₅ O ₃)(H ₂ O)]
Chemical formula	288.04
M_r	Monoclinic, $P2_1/n$
Crystal system, space group	200
Temperature (K)	6.3365 (4), 21.5911 (18), 6.6167 (6)
a, b, c (Å)	100.661 (7)
β (°)	889.62 (12)
V (Å ³)	4
Z	Mo $K\alpha$
Radiation type	4.13
μ (mm ⁻¹)	0.35 × 0.25 × 0.12
Crystal size (mm)	
Data collection	
Diffractometer	Oxford Diffraction Gemini-S CCD-detector
Absorption correction	Multi-scan (CrysAlis PRO; Agilent, 2014)
T_{\min}, T_{\max}	0.758, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3528, 1747, 1466
R_{int}	0.034
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.067, 1.02
No. of reflections	1747
No. of parameters	109
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.76, -0.78

Computer programs: CrysAlis PRO (Agilent, 2014), SIR92 (Altomare *et al.*, 1993), SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 2012), and PLATON (Spek, 2009).

cyate structures, including those of the anhydrous Li salt (Smith *et al.*, 2013), the Li monohydrate salt (Wiesbrock & Schmidbauer, 2003b) and the K and Rb salt (Dinnebier *et al.*, 2002) or salt adducts (Downie & Speakman, 1953), a short intramolecular phenolic O—H \cdots O_{carboxyl} hydrogen bond is present.

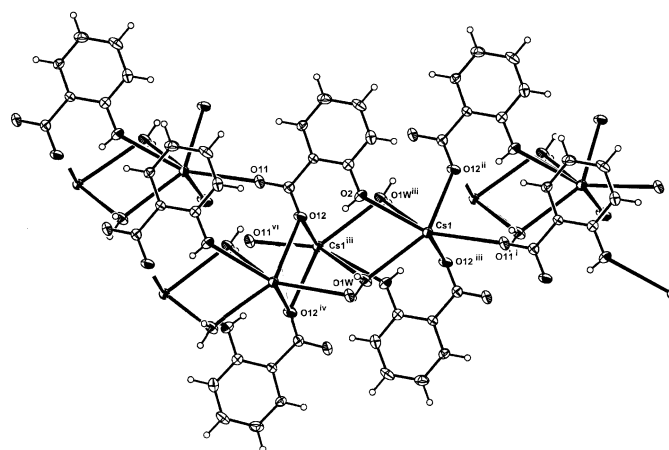


Figure 2
A partial extension of the polymeric structure of the title compound. [Symmetry code: (vi) $-x + 2, -y + 1, -z$; for other codes, see Tables 1 and 2.]

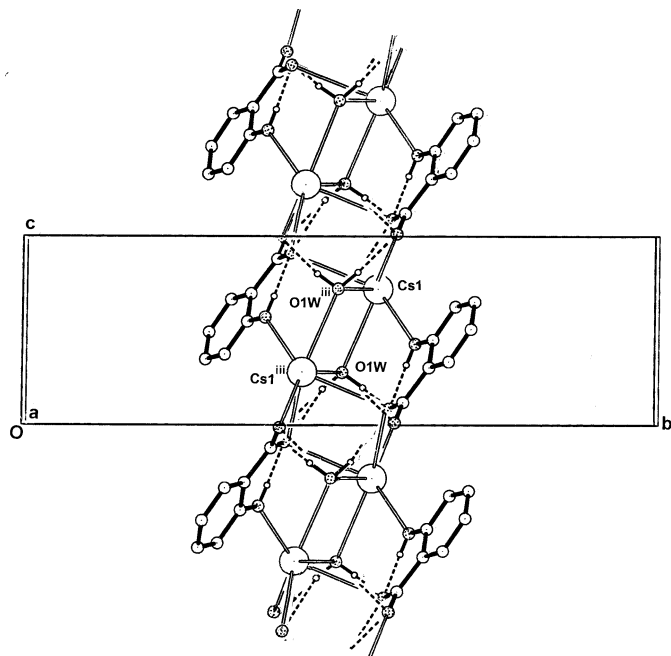


Figure 3

The hydrogen-bonded sheet structure viewed along the *a* axis. Non-associative H atoms are omitted and intramolecular hydrogen bonds are shown as dashed lines.

Synthesis and crystallization

The title compound was formed in the attempted synthesis of a Cs–aspirinate complex by the dropwise addition of cold 50 wt% aqueous caesium hydroxide solution to a solution containing 100 mg of acetylsalicylic acid in 10 ml of 10 wt%

ethanol/water. Room temperature evaporation resulted in a change in the colour of the solution to dark brown, finally giving colourless crystal plates of the title compound from which a specimen was cleaved for the X-ray analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160980 [doi:10.1107/S2414314616009809]

A second monoclinic polymorph of caesium salicylate monohydrate

Graham Smith

Poly[(μ_2 -aqua- μ_4 -(salicylato- κ^4 O¹:O¹:O^{1'}:O²)-caesium)]

Crystal data

[Cs(C₇H₅O₃)(H₂O)]

$M_r = 288.04$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 6.3365$ (4) Å

$b = 21.5911$ (18) Å

$c = 6.6167$ (6) Å

$\beta = 100.661$ (7)°

$V = 889.62$ (12) Å³

$Z = 4$

$F(000) = 544$

$D_x = 2.151$ Mg m⁻³

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

Cell parameters from 1068 reflections

$\theta = 3.4$ – 27.7 °

$\mu = 4.13$ mm⁻¹

$T = 200$ K

Plate, colourless

$0.35 \times 0.25 \times 0.12$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector
diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2014)

$T_{\min} = 0.758$, $T_{\max} = 0.980$

3528 measured reflections

1747 independent reflections

1466 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 3.3$ °

$h = -4 \rightarrow 7$

$k = -25 \rightarrow 26$

$l = -7 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.067$

$S = 1.02$

1747 reflections

109 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 atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.76$ e Å⁻³

$\Delta\rho_{\min} = -0.78$ e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.29377 (5)	0.55788 (1)	0.71890 (4)	0.0318 (1)
O1W	0.2151 (7)	0.50214 (16)	0.2782 (5)	0.0436 (14)
O2	0.5730 (7)	0.61882 (17)	0.4290 (6)	0.0446 (12)
O11	0.9693 (6)	0.59022 (14)	0.0129 (5)	0.0405 (14)
O12	0.6439 (6)	0.58055 (16)	0.0887 (5)	0.0442 (12)
C1	0.8959 (8)	0.64355 (18)	0.3047 (7)	0.0230 (14)
C2	0.7624 (9)	0.64822 (19)	0.4513 (7)	0.0288 (16)
C3	0.8274 (10)	0.6841 (2)	0.6268 (8)	0.0418 (19)
C4	1.0173 (11)	0.7160 (2)	0.6525 (8)	0.045 (2)
C5	1.1508 (10)	0.7116 (2)	0.5083 (8)	0.0441 (19)
C6	1.0884 (8)	0.67583 (19)	0.3357 (7)	0.0307 (16)
C11	0.8343 (9)	0.6023 (2)	0.1204 (7)	0.0293 (16)
H2	0.547 (12)	0.605 (3)	0.318 (9)	0.0670*
H3	0.74190	0.68640	0.72660	0.0500*
H4	1.05740	0.74090	0.76780	0.0540*
H5	1.28100	0.73270	0.52850	0.0530*
H6	1.17670	0.67320	0.23820	0.0370*
H11W	0.183 (10)	0.4708 (19)	0.191 (7)	0.0650*
H12W	0.184 (11)	0.5353 (18)	0.199 (7)	0.0650*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.0266 (2)	0.0422 (2)	0.0263 (2)	−0.0017 (2)	0.0041 (1)	−0.0004 (1)
O1W	0.041 (3)	0.051 (2)	0.034 (2)	0.006 (2)	−0.0055 (19)	−0.0114 (16)
O2	0.029 (2)	0.055 (2)	0.052 (2)	−0.0078 (19)	0.013 (2)	−0.005 (2)
O11	0.050 (3)	0.044 (2)	0.0298 (19)	0.0028 (19)	0.0131 (19)	−0.0068 (16)
O12	0.036 (2)	0.051 (2)	0.042 (2)	−0.0102 (19)	−0.0025 (19)	−0.0136 (17)
C1	0.025 (3)	0.021 (2)	0.021 (2)	0.004 (2)	−0.001 (2)	0.0025 (19)
C2	0.030 (3)	0.024 (2)	0.032 (3)	0.004 (2)	0.005 (2)	0.004 (2)
C3	0.051 (4)	0.042 (3)	0.035 (3)	0.006 (3)	0.015 (3)	−0.002 (2)
C4	0.066 (5)	0.033 (3)	0.031 (3)	−0.005 (3)	−0.005 (3)	−0.009 (2)
C5	0.050 (4)	0.035 (3)	0.044 (3)	−0.014 (3)	0.000 (3)	0.000 (3)
C6	0.030 (3)	0.030 (2)	0.033 (3)	−0.004 (2)	0.008 (2)	0.003 (2)
C11	0.036 (3)	0.027 (2)	0.024 (3)	0.003 (2)	0.003 (2)	0.007 (2)

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

Cs1—O12 ⁱ	3.023 (3)	C1—C11	1.502 (6)
Cs1—O1W	3.108 (3)	C1—C2	1.404 (7)

Cs1—O2	3.130 (4)	C1—C6	1.387 (7)
Cs1—O11 ⁱⁱ	3.159 (4)	C2—C3	1.393 (7)
Cs1—O12 ⁱⁱⁱ	3.244 (3)	C3—C4	1.370 (9)
Cs1—O1W ⁱⁱⁱ	3.368 (4)	C4—C5	1.391 (9)
O2—C2	1.342 (7)	C5—C6	1.375 (7)
O11—C11	1.237 (6)	C3—H3	0.9300
O12—C11	1.275 (7)	C4—H4	0.9300
O1W—H11W	0.89 (4)	C5—H5	0.9300
O1W—H12W	0.89 (4)	C6—H6	0.9300
O2—H2	0.78 (6)		
O1W—Cs1—O2	66.33 (10)	Cs1—O1W—H12W	103 (3)
O1W—Cs1—O11 ⁱⁱ	130.81 (10)	Cs1—O2—H2	112 (5)
O1W—Cs1—O12 ⁱ	142.02 (11)	C2—O2—H2	108 (6)
O1W—Cs1—O1W ⁱⁱⁱ	81.03 (10)	C2—C1—C6	119.2 (4)
O1W—Cs1—O12 ⁱⁱⁱ	89.90 (9)	C2—C1—C11	120.3 (4)
O2—Cs1—O11 ⁱⁱ	142.24 (9)	C6—C1—C11	120.5 (4)
O2—Cs1—O12 ⁱ	90.83 (10)	C1—C2—C3	119.5 (5)
O1W ⁱⁱⁱ —Cs1—O2	62.53 (10)	O2—C2—C1	122.1 (4)
O2—Cs1—O12 ⁱⁱⁱ	125.89 (10)	O2—C2—C3	118.4 (5)
O11 ⁱⁱ —Cs1—O12 ⁱ	85.96 (9)	C2—C3—C4	120.0 (5)
O1W ⁱⁱⁱ —Cs1—O11 ⁱⁱ	141.96 (8)	C3—C4—C5	120.8 (5)
O11 ⁱⁱ —Cs1—O12 ⁱⁱⁱ	90.45 (9)	C4—C5—C6	119.4 (5)
O1W ⁱⁱⁱ —Cs1—O12 ⁱ	61.23 (9)	C1—C6—C5	121.0 (5)
O12 ⁱ —Cs1—O12 ⁱⁱⁱ	79.27 (9)	O11—C11—O12	124.2 (4)
O1W ⁱⁱⁱ —Cs1—O12 ⁱⁱⁱ	66.30 (9)	O11—C11—C1	119.2 (5)
Cs1—O1W—Cs1 ⁱⁱⁱ	98.97 (11)	O12—C11—C1	116.6 (4)
Cs1—O2—C2	136.7 (3)	C2—C3—H3	120.00
Cs1 ^{iv} —O11—C11	177.0 (3)	C4—C3—H3	120.00
Cs1 ^v —O12—C11	136.3 (3)	C3—C4—H4	120.00
Cs1 ⁱⁱⁱ —O12—C11	103.4 (3)	C5—C4—H4	120.00
Cs1 ^v —O12—Cs1 ⁱⁱⁱ	100.74 (10)	C4—C5—H5	120.00
H11W—O1W—H12W	103 (4)	C6—C5—H5	120.00
Cs1 ⁱⁱⁱ —O1W—H11W	79 (4)	C1—C6—H6	119.00
Cs1 ⁱⁱⁱ —O1W—H12W	115 (4)	C5—C6—H6	120.00
Cs1—O1W—H11W	152 (3)		
O2—Cs1—O1W—Cs1 ⁱⁱⁱ	63.85 (11)	Cs1 ^v —O12—C11—C1	139.7 (3)
O11 ⁱⁱ —Cs1—O1W—Cs1 ⁱⁱⁱ	-156.51 (8)	Cs1 ⁱⁱⁱ —O12—C11—O11	79.6 (5)
O12 ⁱ —Cs1—O1W—Cs1 ⁱⁱⁱ	6.24 (19)	Cs1 ⁱⁱⁱ —O12—C11—C1	-98.6 (4)
O1W ⁱⁱⁱ —Cs1—O1W—Cs1 ⁱⁱⁱ	-0.02 (13)	C6—C1—C2—O2	179.1 (4)
O12 ⁱⁱⁱ —Cs1—O1W—Cs1 ⁱⁱⁱ	-66.00 (10)	C6—C1—C2—C3	-1.3 (7)
O1W—Cs1—O2—C2	-153.6 (5)	C11—C1—C2—O2	-3.0 (7)
O11 ⁱⁱ —Cs1—O2—C2	79.6 (5)	C11—C1—C2—C3	176.6 (4)
O12 ⁱ —Cs1—O2—C2	-4.9 (4)	C2—C1—C6—C5	0.7 (7)
O1W ⁱⁱⁱ —Cs1—O2—C2	-61.6 (4)	C11—C1—C6—C5	-177.2 (4)
O12 ⁱⁱⁱ —Cs1—O2—C2	-82.3 (4)	C2—C1—C11—O11	-167.4 (4)
O1W—Cs1—O12 ⁱ —C11 ⁱ	46.9 (5)	C2—C1—C11—O12	10.9 (6)

O2—Cs1—O12 ⁱ —C11 ⁱ	-3.8 (4)	C6—C1—C11—O11	10.5 (6)
O1W—Cs1—O1W ⁱⁱⁱ —Cs1 ⁱⁱⁱ	0.00 (10)	C6—C1—C11—O12	-171.3 (4)
O2—Cs1—O1W ⁱⁱⁱ —Cs1 ⁱⁱⁱ	-67.92 (11)	O2—C2—C3—C4	-178.4 (4)
O1W—Cs1—O12 ⁱⁱⁱ —C11 ⁱⁱⁱ	-73.3 (3)	C1—C2—C3—C4	2.0 (7)
O2—Cs1—O12 ⁱⁱⁱ —C11 ⁱⁱⁱ	-133.5 (3)	C2—C3—C4—C5	-2.1 (8)
Cs1—O2—C2—C1	147.1 (3)	C3—C4—C5—C6	1.5 (7)
Cs1—O2—C2—C3	-32.5 (7)	C4—C5—C6—C1	-0.8 (7)
Cs1 ^v —O12—C11—O11	-42.2 (7)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O12	0.78 (6)	1.82 (6)	2.516 (5)	148 (8)
O1W—H11W \cdots O11 ^{vi}	0.89 (4)	2.00 (5)	2.867 (5)	165 (6)
O1W—H11W \cdots O12 ^{vi}	0.89 (4)	2.57 (5)	3.268 (5)	136 (5)
O1W—H12W \cdots O11 ^{vii}	0.89 (4)	2.04 (5)	2.848 (5)	151 (6)

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