

# Poly[ $\mu_3$ -aqua-aqua( $\mu_3$ -3,5-dinitrobenzoato- $\kappa O^1:O^3:O^5$ )caesium]

Graham Smith

Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia  
Correspondence e-mail: g.smith@qut.edu.au

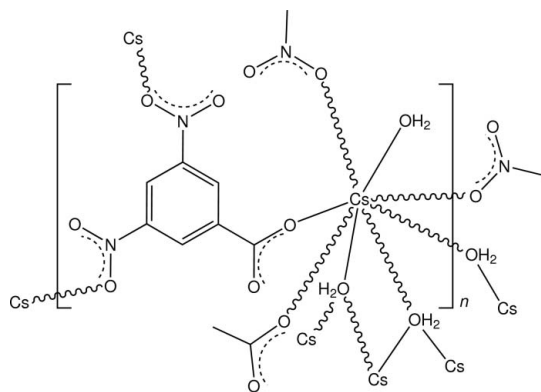
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Key indicators: single-crystal X-ray study;  $T = 200$  K; mean  $\sigma(C-C) = 0.003$  Å;  $R$  factor = 0.024;  $wR$  factor = 0.048; data-to-parameter ratio = 14.8.

In the structure of the title complex,  $[Cs(C_7H_3N_2O_6)(H_2O)_2]_n$ , the Cs salt of 3,5-dinitrobenzoic acid, the metal complex centres have irregular  $CsO_8$  coordination, comprising two water molecules (one triply bridging and the other monodentate) and four O-atom donors from two nitro groups and one bridging carboxylate O-atom donor from the ligand. Intra-unit  $O-H \cdots O$  hydrogen-bonding interactions involving both water molecules are observed in the three-dimensional polymeric complex structure.

## Related literature

For examples of structures of alkali metal complexes with 3,5-dinitrobenzoic acid, see: Yang & Ng (2007) (Li, Na); Tiekink *et al.* (1990); Jones *et al.* (2005); Madej *et al.* (2007) (Na); Miao & Fan (2011); Miao *et al.* (2011) (Rb). For examples of Cs complexes with nitrobenzoic acids, see: Smith & Wermuth (2011a,b).



## Experimental

### Crystal data

$[Cs(C_7H_3N_2O_6)(H_2O)_2]$   
 $M_r = 380.06$   
Monoclinic,  $P2_1/n$   
 $a = 15.1249$  (5) Å  
 $b = 4.6223$  (1) Å  
 $c = 17.1024$  (6) Å

$\beta = 107.782$  (4)°  
 $V = 1138.54$  (7) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation

$\mu = 3.29$  mm<sup>-1</sup>  
 $T = 200$  K  
 $0.28 \times 0.15 \times 0.06$  mm

### Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer  
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)  
 $T_{min} = 0.792$ ,  $T_{max} = 0.980$   
7596 measured reflections  
2652 independent reflections  
2336 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.048$   
 $S = 1.05$   
2652 reflections  
179 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{max} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.56$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Cs1—O1W	3.087 (2)	Cs1—O1W <sup>ii</sup>	3.261 (2)
Cs1—O2W	3.282 (2)	Cs1—O32 <sup>iii</sup>	3.244 (2)
Cs1—O12	3.1751 (16)	Cs1—O1W <sup>iv</sup>	3.346 (2)
Cs1—O12 <sup>i</sup>	3.1120 (17)	Cs1—O52 <sup>v</sup>	3.271 (2)

Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $x, y + 1, z$ ; (iii)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $-x + 1, -y, -z + 2$ ; (v)  $x + \frac{1}{2}, -y - \frac{1}{2}, z + \frac{1}{2}$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H11W $\cdots$ O2W	0.80 (4)	1.98 (4)	2.734 (3)	159 (3)
O1W—H12W $\cdots$ O12 <sup>iv</sup>	0.83 (4)	2.25 (4)	3.016 (3)	155 (4)
O2W—H21W $\cdots$ O11 <sup>vi</sup>	0.83 (4)	1.94 (4)	2.764 (3)	174 (3)
O2W—H22W $\cdots$ O11 <sup>vii</sup>	0.85 (4)	1.96 (4)	2.797 (3)	168 (3)

Symmetry codes: (iv)  $-x + 1, -y, -z + 2$ ; (vi)  $-x + 1, -y + 1, -z + 2$ ; (vii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ .

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5289).

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# metal-organic compounds

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## supporting information

*Acta Cryst.* (2012). E68, m1241–m1242 [https://doi.org/10.1107/S1600536812037130]

**Poly[ $\mu_3$ -aqua-aqua( $\mu_3$ -3,5-dinitrobenzoato- $\kappa O^1:O^3:O^5$ )caesium]****Graham Smith****S1. Comment**

3,5-Dinitrobenzoic acid (DNBA) has been a popular ligand used alone or in mixed-ligand applications for metal complexation and the structures of a large number of its complexes have been reported. With the alkali metals the structures of the complex salts with Li and Na (Yang & Ng, 2007; Jones *et al.*, 2005): the complex salt adduct with Na (Tiekink *et al.*, 1990; Madej *et al.*, 2007) and the Rb complex salt and salt adduct (Miao & Fan, 2011; Miao *et al.*, 2011) are known but the structure of the Cs complex salt has not been reported. The reaction of 3,5-dinitrobenzoic acid with caesium hydroxide in aqueous ethanol gave crystals of the title compound  $[\text{Cs}(\text{C}_7\text{H}_3\text{N}_2\text{O}_6)(\text{H}_2\text{O})_2]_n$  and the structure is reported here. In the Rb and Cs complexes with the nitro-substituted aromatic carboxylic acids, expanded metal coordination spheres together with polymeric structures are common, in which ligands are bridging, *e.g.* anhydrous rubidium 3,5-dinitrobenzoate (8-coordinate) (Miao & Fan, 2011); tetra-caesium bis(5-nitroisophthalate) heptahydrate (6- and 8-coordinate) (Smith & Wermuth, 2011*a*) and caesium bis(2-nitroanthranilate) dihydrate (7- and 9-coordinate) (Smith & Wermuth, 2011*b*).

In the structure of the title compound the  $\text{CsO}_8$  complex unit (Fig. 1) is irregular 8-coordinate [Cs—O range, 3.087 (2)–3.346 (2) Å] (Table 1), comprising two water molecules (one triply bridging, the other monodentate) and four O-donors from two nitro groups and one bridging carboxyl-O donor group from the ligand. In the three-dimensional polymeric complex structure (Fig. 2), the rings of the DNBA ligands layer down the short *b* axis of the unit cell with a ring centroid separation of 4.6223 (1) Å (the *b* cell dimension) (Fig. 3). Present also are intra-polymer O—H $\cdots$ O hydrogen-bonding interactions involving both water molecules (Table 2).

**S2. Experimental**

The title compound was synthesized by heating together under reflux for 10 minutes, 0.5 mmol of caesium hydroxide and 0.5 mmol of 3,5-dinitrobenzoic acid in 20 ml of 10% ethanol–water. Room temperature evaporation of the solution to incipient dryness gave yellow needle crystals of the title complex from which a specimen was cleaved for the X-ray analysis.

**S3. Refinement**

Hydrogen atoms of the coordinated water molecules were located in a difference-Fourier synthesis and both positional and isotropic displacement parameters were allowed to refine. Other H-atoms were included at calculated positions and were allowed to ride, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



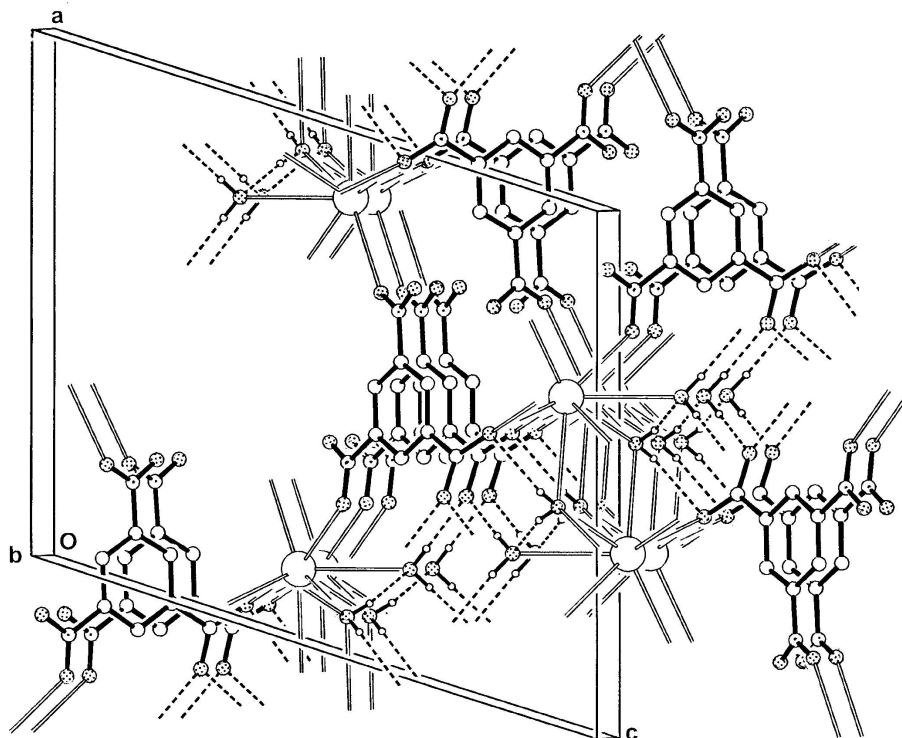


Figure 3

The packing in the unit cell viewed down the the *b* axial direction showing intra-unit hydrogen-bonding associations as dashed lines. Non-interactive H atoms are omitted. For symmetry codes, see Fig. 1 and Table 2.

**Poly[ $\mu_3$ -aqua-aqua( $\mu_3$ -3,5-dinitrobenzoato-  $\kappa O^1:O^3:O^5$ )caesium]**

*Crystal data*

[Cs(C<sub>7</sub>H<sub>3</sub>N<sub>2</sub>O<sub>6</sub>)(H<sub>2</sub>O)<sub>2</sub>]

$M_r = 380.06$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 15.1249$  (5) Å

$b = 4.6223$  (1) Å

$c = 17.1024$  (6) Å

$\beta = 107.782$  (4)°

$V = 1138.54$  (7) Å<sup>3</sup>

$Z = 4$

$F(000) = 728$

$D_x = 2.217$  Mg m<sup>-3</sup>

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

Cell parameters from 3275 reflections

$\theta = 3.2$ – $28.8^\circ$

$\mu = 3.29$  mm<sup>-1</sup>

$T = 200$  K

Needle, yellow

$0.28 \times 0.15 \times 0.06$  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<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2012)

$T_{\min} = 0.792$ ,  $T_{\max} = 0.980$

7596 measured reflections

2652 independent reflections

2336 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 28.9^\circ$ ,  $\theta_{\min} = 3.2^\circ$

$h = -20 \rightarrow 20$

$k = -6 \rightarrow 5$

$l = -22 \rightarrow 22$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.048$   
 $S = 1.05$   
 2652 reflections  
 179 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0172P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.56 \text{ e } \text{\AA}^{-3}$

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 e.s.d.'s 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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.63127 (1)	0.11431 (3)	0.94980 (1)	0.0232 (1)
O1W	0.57824 (16)	-0.3598 (5)	1.05448 (13)	0.0315 (7)
O2W	0.69998 (16)	0.0306 (5)	1.14991 (13)	0.0311 (7)
O11	0.37491 (13)	0.6190 (4)	0.75558 (11)	0.0278 (6)
O12	0.52278 (14)	0.6236 (3)	0.83580 (11)	0.0266 (6)
O31	0.74660 (14)	0.3113 (4)	0.68972 (12)	0.0315 (6)
O32	0.71260 (15)	-0.0756 (4)	0.61600 (12)	0.0351 (7)
O51	0.39421 (16)	-0.3890 (4)	0.51426 (12)	0.0351 (7)
O52	0.28880 (15)	-0.1482 (4)	0.54804 (12)	0.0381 (7)
N3	0.69218 (16)	0.1222 (4)	0.65482 (13)	0.0234 (7)
N5	0.36953 (17)	-0.2001 (5)	0.55368 (12)	0.0246 (7)
C1	0.48439 (18)	0.3386 (5)	0.71545 (14)	0.0169 (7)
C2	0.57543 (18)	0.3203 (5)	0.71383 (14)	0.0177 (7)
C3	0.59685 (18)	0.1317 (5)	0.65956 (15)	0.0186 (7)
C4	0.53156 (19)	-0.0458 (5)	0.60715 (14)	0.0191 (7)
C5	0.44224 (19)	-0.0198 (5)	0.60976 (14)	0.0187 (7)
C6	0.41608 (18)	0.1685 (5)	0.66192 (14)	0.0187 (7)
C11	0.45850 (19)	0.5455 (5)	0.77413 (15)	0.0186 (7)
H2	0.62150	0.43370	0.74890	0.0210*
H4	0.54740	-0.17570	0.57210	0.0230*
H6	0.35450	0.18100	0.66120	0.0220*
H11W	0.616 (3)	-0.280 (7)	1.091 (2)	0.038 (10)*
H12W	0.559 (3)	-0.478 (7)	1.081 (2)	0.055 (12)*
H21W	0.677 (3)	0.124 (6)	1.180 (2)	0.052 (12)*
H22W	0.750 (3)	-0.041 (6)	1.1818 (19)	0.037 (9)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cs1	0.0226 (1)	0.0231 (1)	0.0235 (1)	-0.0002 (1)	0.0063 (1)	0.0030 (1)
O1W	0.0308 (13)	0.0405 (12)	0.0214 (10)	-0.0117 (10)	0.0053 (9)	0.0000 (10)
O2W	0.0259 (12)	0.0355 (11)	0.0284 (11)	0.0046 (10)	0.0032 (10)	-0.0094 (10)
O11	0.0174 (10)	0.0373 (11)	0.0279 (10)	0.0052 (8)	0.0059 (8)	-0.0072 (8)
O12	0.0229 (11)	0.0330 (10)	0.0210 (9)	-0.0005 (8)	0.0023 (8)	-0.0092 (8)
O31	0.0204 (11)	0.0385 (11)	0.0356 (11)	-0.0040 (9)	0.0084 (9)	-0.0042 (9)
O32	0.0310 (12)	0.0442 (12)	0.0324 (11)	0.0130 (9)	0.0130 (10)	-0.0079 (9)
O51	0.0492 (15)	0.0248 (10)	0.0266 (10)	-0.0040 (9)	0.0045 (10)	-0.0093 (8)
O52	0.0252 (12)	0.0548 (13)	0.0342 (11)	-0.0143 (10)	0.0089 (9)	-0.0132 (10)
N3	0.0223 (13)	0.0294 (12)	0.0180 (11)	0.0075 (10)	0.0055 (9)	0.0042 (9)
N5	0.0304 (15)	0.0246 (11)	0.0169 (11)	-0.0075 (10)	0.0044 (10)	-0.0012 (9)
C1	0.0203 (14)	0.0179 (11)	0.0128 (11)	-0.0002 (10)	0.0055 (10)	0.0013 (9)
C2	0.0171 (13)	0.0182 (11)	0.0161 (12)	-0.0004 (10)	0.0024 (10)	0.0025 (10)
C3	0.0188 (14)	0.0198 (12)	0.0178 (12)	0.0039 (10)	0.0067 (10)	0.0057 (10)
C4	0.0278 (15)	0.0153 (11)	0.0141 (12)	0.0013 (10)	0.0063 (10)	-0.0001 (9)
C5	0.0244 (15)	0.0175 (11)	0.0130 (11)	-0.0039 (11)	0.0039 (10)	-0.0005 (10)
C6	0.0197 (14)	0.0207 (12)	0.0152 (11)	-0.0023 (10)	0.0048 (10)	0.0034 (10)
C11	0.0220 (14)	0.0192 (12)	0.0168 (12)	-0.0014 (10)	0.0091 (10)	0.0022 (10)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cs1—O1W	3.087 (2)	O1W—H11W	0.80 (4)
Cs1—O2W	3.282 (2)	O2W—H21W	0.83 (4)
Cs1—O12	3.1751 (16)	O2W—H22W	0.85 (4)
Cs1—O12 <sup>i</sup>	3.1120 (17)	N3—C3	1.469 (4)
Cs1—O1W <sup>ii</sup>	3.261 (2)	N5—C5	1.476 (3)
Cs1—O32 <sup>iii</sup>	3.244 (2)	C1—C2	1.388 (4)
Cs1—O1W <sup>iv</sup>	3.346 (2)	C1—C6	1.395 (3)
Cs1—O52 <sup>v</sup>	3.271 (2)	C1—C11	1.522 (3)
O11—C11	1.253 (4)	C2—C3	1.382 (3)
O12—C11	1.250 (3)	C3—C4	1.382 (4)
O31—N3	1.224 (3)	C4—C5	1.371 (4)
O32—N3	1.224 (3)	C5—C6	1.388 (3)
O51—N5	1.229 (3)	C2—H2	0.9300
O52—N5	1.219 (4)	C4—H4	0.9300
O1W—H12W	0.82 (4)	C6—H6	0.9300
O1W—Cs1—O2W	50.74 (6)	H11W—O1W—H12W	100 (4)
O1W—Cs1—O12	134.87 (6)	Cs1 <sup>i</sup> —O1W—H11W	123 (3)
O1W—Cs1—O12 <sup>i</sup>	70.44 (5)	Cs1 <sup>iv</sup> —O1W—H11W	108 (3)
O1W—Cs1—O1W <sup>ii</sup>	93.43 (6)	Cs1 <sup>i</sup> —O1W—H12W	90 (3)
O1W—Cs1—O32 <sup>iii</sup>	149.39 (6)	Cs1 <sup>iv</sup> —O1W—H12W	75 (3)
O1W—Cs1—O1W <sup>iv</sup>	80.87 (6)	Cs1—O1W—H11W	83 (2)
O1W—Cs1—O52 <sup>v</sup>	60.79 (6)	H21W—O2W—H22W	105 (3)
O2W—Cs1—O12	131.87 (5)	Cs1—O2W—H22W	131 (2)

O2W—Cs1—O12 <sup>i</sup>	120.39 (5)	Cs1—O2W—H21W	122 (2)
O1W <sup>ii</sup> —Cs1—O2W	64.41 (6)	O32—N3—C3	117.8 (2)
O2W—Cs1—O32 <sup>iii</sup>	112.44 (6)	O31—N3—C3	118.5 (2)
O1W <sup>iv</sup> —Cs1—O2W	93.38 (6)	O31—N3—O32	123.7 (3)
O2W—Cs1—O52 <sup>v</sup>	55.78 (6)	O51—N5—O52	124.1 (2)
O12—Cs1—O12 <sup>i</sup>	94.64 (4)	O51—N5—C5	117.8 (2)
O1W <sup>ii</sup> —Cs1—O12	67.47 (5)	O52—N5—C5	118.0 (2)
O12—Cs1—O32 <sup>iii</sup>	75.75 (5)	C6—C1—C11	119.9 (2)
O1W <sup>iv</sup> —Cs1—O12	55.02 (5)	C2—C1—C6	119.5 (2)
O12—Cs1—O52 <sup>v</sup>	164.29 (6)	C2—C1—C11	120.5 (2)
O1W <sup>ii</sup> —Cs1—O12 <sup>i</sup>	135.75 (6)	C1—C2—C3	119.3 (2)
O12 <sup>i</sup> —Cs1—O32 <sup>iii</sup>	113.90 (5)	C2—C3—C4	122.8 (3)
O1W <sup>iv</sup> —Cs1—O12 <sup>i</sup>	85.35 (5)	N3—C3—C2	119.4 (2)
O12 <sup>i</sup> —Cs1—O52 <sup>v</sup>	90.21 (5)	N3—C3—C4	117.7 (2)
O1W <sup>ii</sup> —Cs1—O32 <sup>iii</sup>	100.85 (5)	C3—C4—C5	116.3 (2)
O1W <sup>ii</sup> —Cs1—O1W <sup>iv</sup>	50.88 (6)	C4—C5—C6	123.6 (2)
O1W <sup>ii</sup> —Cs1—O52 <sup>v</sup>	118.15 (5)	N5—C5—C6	118.0 (3)
O1W <sup>iv</sup> —Cs1—O32 <sup>iii</sup>	128.87 (5)	N5—C5—C4	118.4 (2)
O32 <sup>iii</sup> —Cs1—O52 <sup>v</sup>	88.62 (5)	C1—C6—C5	118.4 (3)
O1W <sup>iv</sup> —Cs1—O52 <sup>v</sup>	140.47 (5)	O11—C11—O12	126.9 (2)
Cs1—O1W—Cs1 <sup>i</sup>	93.43 (6)	O11—C11—C1	116.5 (2)
Cs1—O1W—Cs1 <sup>iv</sup>	99.13 (6)	O12—C11—C1	116.6 (2)
Cs1 <sup>i</sup> —O1W—Cs1 <sup>iv</sup>	129.12 (7)	C1—C2—H2	120.00
Cs1—O12—C11	115.28 (13)	C3—C2—H2	120.00
Cs1—O12—Cs1 <sup>ii</sup>	94.64 (5)	C3—C4—H4	122.00
Cs1 <sup>ii</sup> —O12—C11	149.86 (14)	C5—C4—H4	122.00
Cs1 <sup>vi</sup> —O32—N3	148.16 (18)	C1—C6—H6	121.00
Cs1 <sup>vii</sup> —O52—N5	117.78 (15)	C5—C6—H6	121.00
Cs1—O1W—H12W	174 (3)		
O2W—Cs1—O1W—Cs1 <sup>i</sup>	-127.44 (9)	O1W—Cs1—O1W <sup>iv</sup> —Cs1 <sup>iv</sup>	0.00 (6)
O2W—Cs1—O1W—Cs1 <sup>iv</sup>	102.04 (8)	O2W—Cs1—O1W <sup>iv</sup> —Cs1 <sup>iv</sup>	-49.33 (6)
O12—Cs1—O1W—Cs1 <sup>i</sup>	118.81 (6)	O12—Cs1—O1W <sup>iv</sup> —Cs1 <sup>iv</sup>	169.89 (8)
O12—Cs1—O1W—Cs1 <sup>iv</sup>	-11.71 (9)	O1W—Cs1—O52 <sup>v</sup> —N5 <sup>v</sup>	-167.08 (18)
O12 <sup>i</sup> —Cs1—O1W—Cs1 <sup>i</sup>	42.25 (5)	O2W—Cs1—O52 <sup>v</sup> —N5 <sup>v</sup>	-106.86 (18)
O12 <sup>i</sup> —Cs1—O1W—Cs1 <sup>iv</sup>	-88.27 (6)	Cs1—O12—C11—O11	122.9 (2)
O1W <sup>ii</sup> —Cs1—O1W—Cs1 <sup>i</sup>	179.98 (9)	Cs1—O12—C11—C1	-57.0 (3)
O1W <sup>ii</sup> —Cs1—O1W—Cs1 <sup>iv</sup>	49.48 (6)	Cs1 <sup>ii</sup> —O12—C11—O11	-49.7 (5)
O32 <sup>iii</sup> —Cs1—O1W—Cs1 <sup>i</sup>	-61.86 (12)	Cs1 <sup>ii</sup> —O12—C11—C1	130.5 (3)
O32 <sup>iii</sup> —Cs1—O1W—Cs1 <sup>iv</sup>	167.61 (7)	Cs1 <sup>vi</sup> —O32—N3—O31	-0.6 (4)
O1W <sup>iv</sup> —Cs1—O1W—Cs1 <sup>i</sup>	130.53 (6)	Cs1 <sup>vi</sup> —O32—N3—C3	179.48 (19)
O1W <sup>iv</sup> —Cs1—O1W—Cs1 <sup>iv</sup>	-0.02 (12)	Cs1 <sup>vii</sup> —O52—N5—O51	12.2 (3)
O52 <sup>v</sup> —Cs1—O1W—Cs1 <sup>i</sup>	-59.47 (6)	Cs1 <sup>vii</sup> —O52—N5—C5	-169.48 (15)
O52 <sup>v</sup> —Cs1—O1W—Cs1 <sup>iv</sup>	170.01 (8)	O31—N3—C3—C2	-11.0 (3)
O1W—Cs1—O12—C11	-63.1 (2)	O31—N3—C3—C4	167.3 (2)
O1W—Cs1—O12—Cs1 <sup>ii</sup>	113.15 (7)	O32—N3—C3—C2	169.0 (2)
O2W—Cs1—O12—C11	-135.23 (18)	O32—N3—C3—C4	-12.7 (3)
O2W—Cs1—O12—Cs1 <sup>ii</sup>	41.03 (9)	O51—N5—C5—C4	8.4 (3)



O12 <sup>i</sup> —Cs1—O12—C11	3.7 (2)	O51—N5—C5—C6	-172.0 (2)
O12 <sup>i</sup> —Cs1—O12—Cs1 <sup>ii</sup>	-180.00 (7)	O52—N5—C5—C4	-170.0 (2)
O1W <sup>ii</sup> —Cs1—O12—C11	-134.4 (2)	O52—N5—C5—C6	9.6 (3)
O1W <sup>ii</sup> —Cs1—O12—Cs1 <sup>ii</sup>	41.90 (6)	C6—C1—C2—C3	-0.5 (3)
O32 <sup>iii</sup> —Cs1—O12—C11	117.2 (2)	C11—C1—C2—C3	-179.6 (2)
O32 <sup>iii</sup> —Cs1—O12—Cs1 <sup>ii</sup>	-66.50 (5)	C2—C1—C6—C5	1.5 (3)
O1W <sup>iv</sup> —Cs1—O12—C11	-77.3 (2)	C11—C1—C6—C5	-179.4 (2)
O1W <sup>iv</sup> —Cs1—O12—Cs1 <sup>ii</sup>	98.99 (7)	C2—C1—C11—O11	158.1 (2)
O1W—Cs1—O12 <sup>i</sup> —Cs1 <sup>i</sup>	-43.76 (6)	C2—C1—C11—O12	-22.1 (3)
O1W—Cs1—O12 <sup>i</sup> —C11 <sup>i</sup>	129.5 (4)	C6—C1—C11—O11	-21.0 (3)
O2W—Cs1—O12 <sup>i</sup> —Cs1 <sup>i</sup>	-34.52 (8)	C6—C1—C11—O12	158.9 (2)
O2W—Cs1—O12 <sup>i</sup> —C11 <sup>i</sup>	138.7 (4)	C1—C2—C3—N3	177.0 (2)
O12—Cs1—O12 <sup>i</sup> —Cs1 <sup>i</sup>	180.00 (7)	C1—C2—C3—C4	-1.2 (4)
O12—Cs1—O12 <sup>i</sup> —C11 <sup>i</sup>	-6.8 (4)	N3—C3—C4—C5	-176.4 (2)
O1W—Cs1—O1W <sup>ii</sup> —Cs1 <sup>ii</sup>	179.98 (9)	C2—C3—C4—C5	1.9 (4)
O2W—Cs1—O1W <sup>ii</sup> —Cs1 <sup>ii</sup>	137.03 (8)	C3—C4—C5—N5	178.7 (2)
O12—Cs1—O1W <sup>ii</sup> —Cs1 <sup>ii</sup>	-42.25 (5)	C3—C4—C5—C6	-0.9 (4)
O1W—Cs1—O32 <sup>iii</sup> —N3 <sup>iii</sup>	-174.4 (3)	N5—C5—C6—C1	179.7 (2)
O2W—Cs1—O32 <sup>iii</sup> —N3 <sup>iii</sup>	-124.7 (3)	C4—C5—C6—C1	-0.8 (4)
O12—Cs1—O32 <sup>iii</sup> —N3 <sup>iii</sup>	5.1 (3)		

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $x, y+1, z$ ; (iii)  $-x+3/2, y+1/2, -z+3/2$ ; (iv)  $-x+1, -y, -z+2$ ; (v)  $x+1/2, -y-1/2, z+1/2$ ; (vi)  $-x+3/2, y-1/2, -z+3/2$ ; (vii)  $x-1/2, -y-1/2, z-1/2$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H11W $\cdots$ O2W	0.80 (4)	1.98 (4)	2.734 (3)	159 (3)
O1W—H12W $\cdots$ O12 <sup>iv</sup>	0.83 (4)	2.25 (4)	3.016 (3)	155 (4)
O2W—H21W $\cdots$ O11 <sup>viii</sup>	0.83 (4)	1.94 (4)	2.764 (3)	174 (3)
O2W—H22W $\cdots$ O11 <sup>ix</sup>	0.85 (4)	1.96 (4)	2.797 (3)	168 (3)

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