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Crystal structure of poly[[di-μ_2-aqua-aquasodium] 4-amino-3,5,6-trichloropyridine-2-carboxylate trihydrate], the sodium salt of the herbicide picloram

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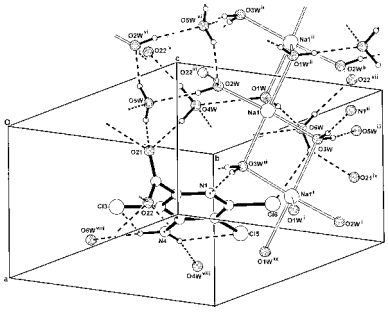
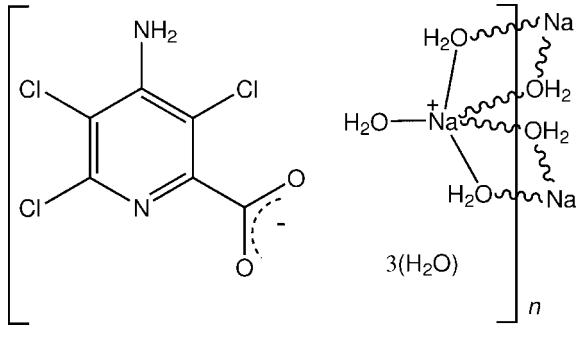
In the structure of the title complex, $\{[Na(H_2O)_3](C_6H_2Cl_3N_2O_2)\cdot 3H_2O\}_n$, the sodium salt of the herbicide picloram, the cation adopts a polymeric chain structure, based on μ_2-aqua-bridged NaO_5 trigonal–bipyramidal complex units which have, in addition, a singly bonded water molecule. Each of the bridges within the chain, which extends parallel to the *a* axis, is centrosymmetric, with Na···Na separations of 3.4807 (16) and 3.5109 (16) Å. In the crystal, there are three water molecules of solvation and these, as well as the coordinating water molecules and the amino group of the 4-amino-3,5,6-trichloropicolinate anion, are involved in extensive inter-species hydrogen-bonding interactions with carboxyl and water O atoms, as well as the pyridine N atom. Among these associations is a centrosymmetric cyclic tetrawater $R_4^4(8)$ motif, resulting in an overall three-dimensional structure.

1. Chemical context

4-Amino-3,5,6-trichloropyridine-2-carboxylic acid (picloram) is a commercial herbicide (Mullinson, 1985) introduced by Dow Chemicals as Tordon (O'Neil, 2001). Although it has potential as a metal-chelating ligand similar to picolinic acid, there are only five metal complexes with picloramate anions in the crystallographic literature. Examples include picloram as a bidentate *N,O* chelating ligand with Mn^{II} (Smith *et al.*, 1981*a*) and Cu^{II} (two structures, one a mixed-ligand complex with 2-aminopyrimidine; O'Reilly *et al.*, 1983) and caesium (Smith, 2013). In the Mg complex (Smith *et al.*, 1981*b*), the picloramate anions act as counter-ions to the $[Mg(H_2O)_6]^{2+}$ cation. Although the structure of picloram has not been reported, that of the guanidinium salt is known (Parthasarathi *et al.*, 1982). The reaction of picloram with sodium bicarbonate in aqueous ethanol gave crystals of the title complex salt $\{[Na(H_2O)_3]^+\cdot C_6H_2Cl_3N_2O_2^-\cdot 3H_2O\}_n$, and the structure is reported herein.





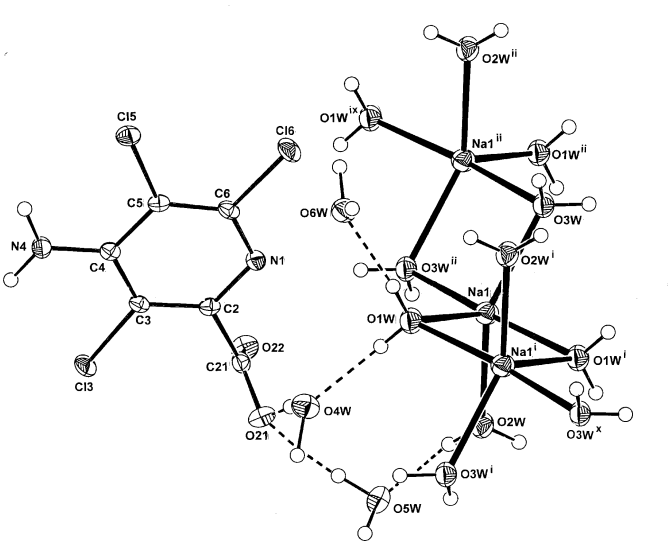


Figure 1
The atom-numbering scheme for the hydrated title salt, with non-H atoms drawn as 40% probability ellipsoids. Inter-species hydrogen bonds are shown as dashed lines. Symmetry codes: (ix) $x+1, y, z$; (x) $x-1, y, z$. For other symmetry codes, see Table 1.

2. Structural commentary

In the structure of the title salt, (Fig. 1), polymeric cationic chains based on μ_2-water-bridged NaO_5 trigonal–bipyramidal complex units are formed, comprising centrosymmetric four-membered water-bridged Na_2O_2 rings with both O1*W* and O3*W* [Na···Na^{i} and Na···Na^{ii} = 3.4807 (16) and 3.5109 (16) Å, respectively; for symmetry codes, see Table 1]. In the fifth Na coordination site is the third water molecule (O2*W*) in a non-bridging mode [overall Na—O range, 2.3183 (17)–2.4185 (16) Å: Table 1]. Although the μ_2-water-bridged cationic chains are relatively common, the NaO_5 coordination with one non-bridging water is rare, compared to the more usual octahedral NaO_6 coordination involving two non-bridging water molecules in other examples, *e.g.* in the biphenyl-4,4′-diphosphonate salt (Kinnibrugh *et al.*, 2012).

The structure of the title salt also contains non-coordinating picloramate anions and three water molecules of solvation (O4*W*–O6*W*). In this anion, the carboxyl group lies close to perpendicular to the pyridine ring [torsion angle N1—C2—C21—O21 = 89.1 (2)°], which is similar to that in the anhydrous guanidinium picloramate salt (73.3°) (Parthasarathi *et al.*, 1982), while the amine group gives lateral intramolecular N4—H41···Cl3 and N4—H41···O6*W* interactions [2.9956 (17), 3.080 (2) Å].

Table 1
Selected bond lengths (Å).

Na1—O1*W*^{i}	2.4185 (16)	Na1—O2*W*	2.3183 (17)
Na1—O3*W*^{ii}	2.3803 (16)	Na1—O3*W*	2.3530 (16)
Na1—O1*W*	2.3529 (16)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O4*W*	0.82	1.97	2.786 (2)	178
O1*W*—H12*W*···O6*W*	0.89	1.99	2.877 (2)	174
O2*W*—H21*W*···O22^{iii}	0.94	1.79	2.721 (2)	171
O2*W*—H22*W*···O5*W*	0.84	1.98	2.816 (2)	172
O3*W*—H31*W*···O5*W*^{iv}	0.88	1.93	2.781 (2)	163
O3*W*—H32*W*···N1^{ii}	0.90	2.02	2.910 (2)	170
O4*W*—H41*W*···O22^{v}	0.99	1.93	2.916 (2)	173
O4*W*—H42*W*···O21	0.93	1.99	2.918 (2)	174
O5*W*—H51*W*···O21	0.90	1.87	2.748 (2)	166
O5*W*—H52*W*···O2*W*^{vi}	0.90	2.01	2.8481 (19)	155
O6*W*—H61*W*···O22^{vii}	0.93	2.10	2.972 (2)	156
O6*W*—H62*W*···O21^{iv}	0.93	2.19	2.996 (2)	144
N4—H41···O6*W*^{viii}	0.96	2.18	3.080 (2)	156
N4—H42···O4*W*^{viii}	0.97	2.22	3.146 (2)	160

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

3. Supramolecular features

In the crystal there are numerous inter-species water O—H···O$_{carboxyl,water}$, O—H···N$_{pyridine}$ and O—H···Cl hydrogen-bonding interactions (Table 2), including a centrosymmetric tetra-water cyclic ring involving O2*W*—H···O5*W* and O5*W*—H···O2*W*^{vi} [graph set $R_4^4(8)$], giving a three-dimensional structure (Fig. 2). Cyclic tetra-water moieties such as found in the present structure are being identified in an increasing number in labile water-stabilized salt hydrates, *e.g.* in the brucinium L-glycerate 4.75-hydrate salt (Białońska *et al.*, 2005). Also found in the structure of the title salt is a short intermolecular Cl3···Cl5^{xi} contact [3.2108 (7) Å; symmetry code (xi): $x, y-1, z$].

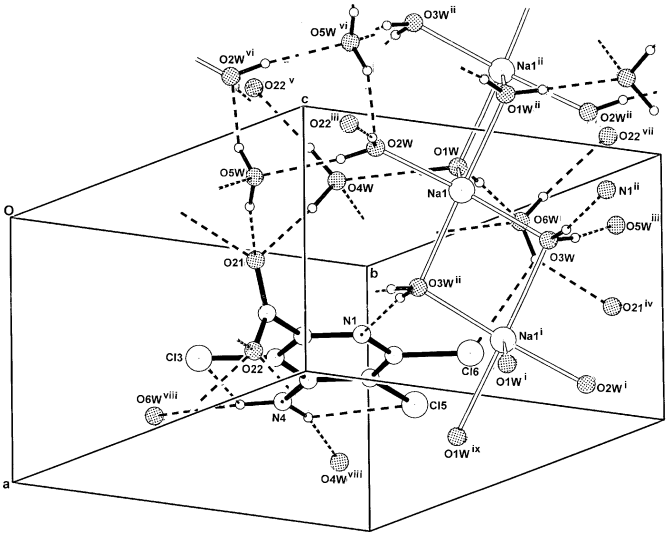


Figure 2
The three-dimensional hydrogen-bonded structure, with inter-species hydrogen bonds and intramolecular N—H···Cl associations shown as dashed lines. For symmetry codes, see Fig. 1 and Table 2.

4. Database survey

The (μ_2-aqua)-bridged $Na_2(H_2O)_2$ units in the coordination polymeric cationic chains in the title structure have precedents

in a large number of reported crystal structures. However, with few exceptions, these are based on NaO_6 polyhedra, with octahedral or distorted octahedral stereochemistry, having two non-bridging water molecules $[Na_2(H_2O)_8^{2+}]$, compared to one non-bridging water molecule in the NaO_5 coordination $[Na_2(H_2O)_6^{2+}]$ of the title complex. The $[Na_2(H_2O)_8^{2+}]$ dications may be discrete, such as found in the anionic aryltelluronic anhydride salt (Beckmann *et al.*, 2012) and the anionic dimethylarsenate (cacodylate) salt (Lennartson & Håkansson, 2008), or they may be found as $[Na_4(H_2O)_{16}^{4+}]$ tetra-cations as found in the dianionic biphenyl-4,4′-diphosphonate salt (Kinnibrugh *et al.*, 2012) and the monoanionic salt of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione; Guzei *et al.*, 2013). However, more commonly, they are polymeric $[Na_2(H_2O)_8]_n$, *e.g.* in the monoanionic salt of the anti-allergic drug tranilast ({2-[3-(3,4-dimethoxyphenyl)acrolyl]amino}benzoic acid; Geng *et al.*, 2013), but often associated with metal complex anions, *e.g.* the Cu^{II} complex with pyrophosphate, $[Cu(H_2O)(phen)(P_2O_7)]^{2-}$ (phen = 1,10-phenanthroline; Marino *et al.*, 2010), the mixed-valent di-$Ru^{II,III}$ complex with 1-hydroxyethane 1,1-diphosphonate (hedp) $[Ru_2(hedp)_2X]^{4-}$ (X = Cl, Br; Yi *et al.*, 2005) and the dioxo-Np complex anion salt with dipicolinate (dipic), $[NpO_2(dipic)(H_2O)_2]^-$ (Tian *et al.*, 2009).

5. Synthesis and crystallization

The title compound was synthesized by briefly heating together 0.5 mmol of 4-amino-3,5,6-trichloropicolinic acid (picloram) with excess $NaHCO_3$ in 10 ml of 10% (*v*/*v*) ethanol–water. Room temperature evaporation of the solution to dryness gave minor colourless crystal blocks of the title complex from which a specimen was cleaved for the X-ray analysis.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms of the water molecules and the amine group were located in a difference-Fourier synthesis but were subsequently constrained in the refinement with the isotropic displacement parameters allowed to ride, with $U_{iso}(H) = 1.2U_{eq}(N)$ or $1.5U_{eq}(O)$.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Na(H_2O)_3](C_6H_2Cl_3N_2O_2)\cdot 3H_2O$
M_r	371.53
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	200
a, b, c (Å)	6.5625 (5), 8.4574 (6), 13.8553 (10)
α, β, γ (°)	78.747 (6), 79.374 (6), 88.864 (6)
V (Å^3)	741.17 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.68
Crystal size (mm)	0.35 × 0.35 × 0.22
Data collection	
Diffractometer	Oxford Diffraction Gemini-S CCD detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.947, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6040, 2905, 2487
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.088, 1.00
No. of reflections	2905
No. of parameters	182
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.28

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

Acknowledgements

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supporting information

Acta Cryst. (2015). E**71**, 931-933 [https://doi.org/10.1107/S2056989015012633]

Crystal structure of poly[[di-μ_2-aqua-aquasodium] 4-amino-3,5,6-trichloropyridine-2-carboxylate trihydrate], the sodium salt of the herbicide picloram

Graham Smith

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

Poly[[di-μ_2-aqua-aquasodium] 4-amino-3,5,6-trichloropyridine-2-carboxylate trihydrate]

Crystal data

$[Na(H_2O)_3](C_6H_2Cl_3N_2O_2)\cdot 3H_2O$
$M_r = 371.53$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.5625$ (5) Å
$b = 8.4574$ (6) Å
$c = 13.8553$ (10) Å
$\alpha = 78.747$ (6)°
$\beta = 79.374$ (6)°
$\gamma = 88.864$ (6)°
$V = 741.17$ (9) Å^3
$Z = 2$
$F(000) = 380$
$D_x = 1.665$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2548 reflections
$\theta = 3.8$–28.8°
$\mu = 0.68$ mm^{-1}
$T = 200$ K
Block, colourless
0.35 × 0.35 × 0.22 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)
$T_{min} = 0.947$, $T_{max} = 0.980$
6040 measured reflections
2905 independent reflections
2487 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.3°$
$h = -8\rightarrow 7$
$k = -10\rightarrow 10$
$l = -17\rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.088$
$S = 1.00$
2905 reflections
182 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

$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.2264P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 2012)
Extinction coefficient: 0.050 (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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl3	0.73580 (8)	0.09272 (5)	0.52593 (4)	0.0257 (2)
Cl5	0.76678 (8)	0.74102 (5)	0.46993 (4)	0.0240 (2)
Cl6	0.67863 (9)	0.70381 (6)	0.70472 (4)	0.0295 (2)
O21	0.4767 (2)	0.04778 (17)	0.77535 (11)	0.0287 (5)
O22	0.8188 (2)	0.04407 (17)	0.77067 (11)	0.0292 (5)
N1	0.6684 (2)	0.39495 (18)	0.71307 (12)	0.0196 (5)
N4	0.7849 (3)	0.42747 (19)	0.40294 (12)	0.0213 (5)
C2	0.6814 (3)	0.2631 (2)	0.67196 (14)	0.0172 (5)
C3	0.7193 (3)	0.2696 (2)	0.57064 (14)	0.0170 (5)
C4	0.7473 (3)	0.4178 (2)	0.50250 (14)	0.0168 (6)
C5	0.7335 (3)	0.5539 (2)	0.54712 (14)	0.0173 (5)
C6	0.6946 (3)	0.5361 (2)	0.64975 (15)	0.0186 (6)
C21	0.6561 (3)	0.1034 (2)	0.74534 (14)	0.0204 (6)
Na1	0.24455 (12)	0.42819 (9)	1.01558 (6)	0.0268 (3)
O1W	0.0817 (2)	0.53070 (17)	0.87914 (10)	0.0299 (5)
O2W	0.1503 (2)	0.15728 (17)	1.05390 (11)	0.0300 (5)
O3W	0.4202 (2)	0.62279 (17)	1.07140 (10)	0.0272 (5)
O4W	0.1371 (2)	0.27585 (17)	0.77676 (12)	0.0317 (5)
O5W	0.2700 (2)	−0.10534 (18)	0.95986 (11)	0.0325 (5)
O6W	0.1709 (2)	0.82429 (17)	0.73270 (11)	0.0298 (5)
H41	0.80460	0.32820	0.37840	0.0260*
H42	0.80680	0.53330	0.36040	0.0260*
H11W	0.09740	0.45450	0.85000	0.0450*
H12W	0.10510	0.62480	0.83710	0.0450*
H21W	0.15180	0.09520	1.11820	0.0450*
H22W	0.19310	0.08550	1.02150	0.0450*
H31W	0.38250	0.71930	1.04480	0.0410*
H32W	0.40980	0.61800	1.13770	0.0410*
H41W	0.02360	0.20490	0.77150	0.0480*
H42W	0.25100	0.20920	0.77350	0.0480*
H51W	0.34890	−0.07030	0.89970	0.0490*
H52W	0.15590	−0.13130	0.93860	0.18 (2)*

H61W	0.06160	0.89510	0.72480	0.0450*
H62W	0.30130	0.87260	0.72460	0.0450*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl3	0.0359 (3)	0.0159 (2)	0.0269 (3)	0.0007 (2)	−0.0044 (2)	−0.0091 (2)
Cl5	0.0280 (3)	0.0146 (2)	0.0282 (3)	−0.0001 (2)	−0.0049 (2)	−0.0012 (2)
Cl6	0.0412 (3)	0.0196 (3)	0.0309 (3)	0.0023 (2)	−0.0063 (2)	−0.0131 (2)
O21	0.0247 (8)	0.0260 (8)	0.0314 (9)	−0.0065 (6)	−0.0013 (6)	0.0013 (6)
O22	0.0290 (8)	0.0250 (8)	0.0318 (9)	0.0043 (6)	−0.0089 (7)	0.0013 (6)
N1	0.0202 (9)	0.0195 (8)	0.0195 (9)	0.0004 (6)	−0.0025 (7)	−0.0060 (7)
N4	0.0263 (9)	0.0197 (8)	0.0178 (8)	0.0009 (7)	−0.0031 (7)	−0.0042 (6)
C2	0.0128 (9)	0.0164 (9)	0.0220 (10)	0.0008 (7)	−0.0024 (7)	−0.0037 (7)
C3	0.0152 (9)	0.0147 (9)	0.0224 (10)	0.0005 (7)	−0.0038 (7)	−0.0063 (7)
C4	0.0106 (9)	0.0193 (10)	0.0216 (10)	0.0008 (7)	−0.0044 (7)	−0.0053 (8)
C5	0.0141 (9)	0.0144 (9)	0.0228 (10)	0.0002 (7)	−0.0041 (7)	−0.0019 (7)
C6	0.0160 (10)	0.0167 (9)	0.0252 (10)	0.0015 (7)	−0.0040 (8)	−0.0090 (8)
C21	0.0251 (11)	0.0192 (9)	0.0177 (10)	0.0014 (8)	−0.0028 (8)	−0.0068 (7)
Na1	0.0249 (5)	0.0264 (4)	0.0291 (5)	−0.0002 (3)	−0.0031 (3)	−0.0068 (3)
O1W	0.0360 (9)	0.0275 (8)	0.0252 (8)	0.0022 (6)	−0.0021 (7)	−0.0065 (6)
O2W	0.0390 (9)	0.0239 (8)	0.0246 (8)	0.0020 (6)	−0.0008 (7)	−0.0039 (6)
O3W	0.0322 (9)	0.0264 (8)	0.0223 (8)	0.0022 (6)	−0.0020 (6)	−0.0064 (6)
O4W	0.0282 (8)	0.0283 (8)	0.0399 (9)	0.0023 (6)	−0.0067 (7)	−0.0097 (7)
O5W	0.0342 (9)	0.0353 (9)	0.0247 (8)	0.0009 (7)	−0.0010 (7)	−0.0020 (7)
O6W	0.0257 (8)	0.0311 (8)	0.0330 (9)	−0.0003 (6)	−0.0043 (7)	−0.0079 (6)

Geometric parameters (Å, º)

Na1—O1W^{i}	2.4185 (16)	O4W—H42W	0.9300
Na1—O3W^{ii}	2.3803 (16)	O4W—H41W	0.9900
Na1—O1W	2.3529 (16)	O5W—H52W	0.9000
Na1—O2W	2.3183 (17)	O5W—H51W	0.9000
Na1—O3W	2.3530 (16)	O6W—H61W	0.9300
Cl3—C3	1.7216 (18)	O6W—H62W	0.9300
Cl5—C5	1.7213 (18)	N1—C2	1.342 (2)
Cl6—C6	1.7289 (19)	N1—C6	1.330 (2)
O21—C21	1.243 (2)	N4—C4	1.342 (2)
O22—C21	1.250 (2)	N4—H41	0.9600
O1W—H12W	0.8900	N4—H42	0.9700
O1W—H11W	0.8200	C2—C3	1.370 (3)
O2W—H21W	0.9400	C2—C21	1.515 (3)
O2W—H22W	0.8400	C3—C4	1.407 (3)
O3W—H31W	0.8800	C4—C5	1.403 (2)
O3W—H32W	0.9000	C5—C6	1.376 (3)
O1W^{i}—Na1—O3W^{ii}	173.66 (6)	H41W—O4W—H42W	103.00
O1W—Na1—O3W	114.69 (6)	H51W—O5W—H52W	98.00

O1W—Na1—O1W^{i}	86.32 (5)	H61W—O6W—H62W	116.00
O1W—Na1—O3W^{ii}	100.02 (6)	C2—N1—C6	116.35 (16)
O2W—Na1—O3W	141.97 (6)	C4—N4—H41	118.00
O1W^{i}—Na1—O2W	85.88 (6)	C4—N4—H42	118.00
O2W—Na1—O3W^{ii}	92.71 (6)	H41—N4—H42	124.00
O1W—Na1—O2W	103.20 (6)	N1—C2—C3	123.14 (17)
O3W—Na1—O3W^{ii}	84.24 (5)	N1—C2—C21	115.53 (16)
O1W^{i}—Na1—O3W	93.06 (5)	C3—C2—C21	121.32 (16)
Na1—O1W—Na1^{i}	93.68 (5)	Cl3—C3—C2	119.28 (14)
Na1—O3W—Na1^{ii}	95.76 (6)	Cl3—C3—C4	119.39 (14)
Na1—O1W—H11W	100.00	C2—C3—C4	121.32 (16)
Na1^{i}—O1W—H11W	121.00	N4—C4—C3	122.49 (16)
Na1—O1W—H12W	128.00	N4—C4—C5	122.95 (17)
H11W—O1W—H12W	112.00	C3—C4—C5	114.55 (17)
Na1^{i}—O1W—H12W	103.00	Cl5—C5—C4	118.07 (14)
Na1—O2W—H22W	128.00	Cl5—C5—C6	121.71 (14)
H21W—O2W—H22W	97.00	C4—C5—C6	120.22 (16)
Na1—O2W—H21W	121.00	Cl6—C6—N1	115.37 (15)
Na1—O3W—H32W	119.00	Cl6—C6—C5	120.21 (14)
H31W—O3W—H32W	108.00	N1—C6—C5	124.42 (17)
Na1—O3W—H31W	109.00	O21—C21—O22	127.24 (18)
Na1^{ii}—O3W—H32W	115.00	O21—C21—C2	116.83 (17)
Na1^{ii}—O3W—H31W	109.00	O22—C21—C2	115.91 (17)

O3W^{ii}—Na1—O3W—Na1^{ii}	0.00 (6)	N1—C2—C21—O21	89.1 (2)
O1W—Na1—O1W^{i}—Na1^{i}	0.00 (6)	N1—C2—C3—Cl3	179.26 (15)
O2W—Na1—O1W^{i}—Na1^{i}	−103.53 (6)	N1—C2—C3—C4	0.0 (3)
O3W—Na1—O1W^{i}—Na1^{i}	114.57 (6)	C21—C2—C3—Cl3	0.7 (3)
O1W—Na1—O3W^{ii}—Na1^{ii}	114.11 (6)	C3—C2—C21—O22	89.4 (2)
O2W—Na1—O3W^{ii}—Na1^{ii}	−141.98 (6)	N1—C2—C21—O22	−89.3 (2)
O3W—Na1—O3W^{ii}—Na1^{ii}	−0.02 (8)	C3—C2—C21—O21	−92.2 (2)
O2W—Na1—O3W—Na1^{ii}	87.03 (10)	C2—C3—C4—C5	0.1 (3)
O1W^{i}—Na1—O3W—Na1^{ii}	174.25 (5)	Cl3—C3—C4—N4	0.6 (3)
O2W—Na1—O1W—Na1^{i}	84.89 (6)	Cl3—C3—C4—C5	−179.13 (15)
O3W—Na1—O1W—Na1^{i}	−91.68 (6)	C2—C3—C4—N4	179.9 (2)
O1W^{i}—Na1—O1W—Na1^{i}	0.00 (5)	C3—C4—C5—Cl5	179.71 (15)
O3W^{ii}—Na1—O1W—Na1^{i}	−179.91 (5)	N4—C4—C5—Cl5	−0.1 (3)
O1W—Na1—O3W—Na1^{ii}	−98.40 (6)	N4—C4—C5—C6	−180.0 (2)
C6—N1—C2—C21	178.63 (17)	C3—C4—C5—C6	−0.2 (3)
C2—N1—C6—Cl6	−179.62 (14)	C4—C5—C6—N1	0.2 (3)
C6—N1—C2—C3	0.0 (3)	Cl5—C5—C6—Cl6	−0.2 (3)
C2—N1—C6—C5	−0.1 (3)	Cl5—C5—C6—N1	−179.72 (15)
C21—C2—C3—C4	−178.59 (18)	C4—C5—C6—Cl6	179.74 (16)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O4*W*	0.82	1.97	2.786 (2)	178
O1*W*—H12*W*···O6*W*	0.89	1.99	2.877 (2)	174
O2*W*—H21*W*···O22^{iii}	0.94	1.79	2.721 (2)	171
O2*W*—H22*W*···O5*W*	0.84	1.98	2.816 (2)	172
O3*W*—H31*W*···O5*W*^{iv}	0.88	1.93	2.781 (2)	163
O3*W*—H32*W*···N1^{ii}	0.90	2.02	2.910 (2)	170
O4*W*—H41*W*···O22^{v}	0.99	1.93	2.916 (2)	173
O4*W*—H42*W*···O21	0.93	1.99	2.918 (2)	174
O5*W*—H51*W*···O21	0.90	1.87	2.748 (2)	166
O5*W*—H52*W*···O2*W*^{vi}	0.90	2.01	2.8481 (19)	155
O6*W*—H61*W*···O22^{vii}	0.93	2.10	2.972 (2)	156
O6*W*—H62*W*···Cl6	0.93	2.83	3.4400 (15)	124
O6*W*—H62*W*···O21^{iv}	0.93	2.19	2.996 (2)	144
N4—H41···Cl3	0.96	2.54	2.9956 (17)	109
N4—H41···O6*W*^{viii}	0.96	2.18	3.080 (2)	156
N4—H42···Cl5	0.97	2.52	2.9690 (17)	108
N4—H42···O4*W*^{viii}	0.97	2.22	3.146 (2)	160

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+2; (iii) −*x*+1, −*y*, −*z*+2; (iv) *x*, *y*+1, *z*; (v) *x*−1, *y*, *z*; (vi) −*x*, −*y*, −*z*+2; (vii) *x*−1, *y*+1, *z*; (viii) −*x*+1, −*y*+1, −*z*+1.