Poly[(μ₆-4-amino-3,5,6-trichloropyridine-2-carboxylato)aqua-caesium]

Graham Smith

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Poly[(\(\mu_6\)-4-amino-3,5,6-trichloropyridine-2-carboxylato)aquacæsium]  

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Key indicators: single-crystal X-ray study; \(T = 200\) K; mean \(\sigma(C–C) = 0.005\) Å; \(R\) factor = 0.021; \(wR\) factor = 0.053; data-to-parameter ratio = 13.1.  

In the structure of the title complex, \([\text{Cs}(\text{C}_6\text{H}_2\text{Cl}_3\text{N}_2\text{O}_2)(\text{H}_2\text{O})]\)_n, the caesium salt of the commercial herbicide picloram, the Cs\(^+\) cation lies on a crystallographic mirror plane, which also contains the coordinating water molecule and all non-H atoms of the 4-amino-3,5,6-trichloropicolinate anion except the carboxylate O-atom donors. The irregular CsCl\(_2\)O\(_5\) coordination polyhedron comprises chlorine donors from the \(ortho\)-related ring substituents of the picloramate ligand in a bidentate chelate mode, with a third chlorine bridging [Cs—Cl range 3.6052 (11)—3.7151 (11) Å] as well as a bidentate chelate carboxylate group giving sheets extending parallel to (010). A three-dimensional coordination polymer structure is generated through the carboxylate group, which also bridges the sheets down [010]. Within the structure, there are intra-unit water O—H...O(carboxylate) and amine N—H...N(pyr)idine hydrogen-bonding interactions.  

Related literature  

For background information on picloram, see: Mullinson (1985); O’Neil (2001). For examples of structures of metal complexes with picloram, see: Smith et al. (1981a,b); O’Reilly et al. (1983). For another structure with caesium cations involving coordinating carbon-bound Cl, see: Levitskaia et al. (2000). For a caesium complex with dipicolinic acid, see: Santra et al. (2011).  

Experimental  

Crystal data  

\[
\text{[Cs(C}_6\text{H}_2\text{Cl}_3\text{N}_2\text{O}_2)(\text{H}_2\text{O})]} \quad V = 545.58 (4) \text{ Å}^3 \]  

\(Z = 2\)  

Monoclinic, \(P_2_1/m\)  

\(a = 7.0816 (3)\) Å  

\(b = 6.6863 (2)\) Å  

\(c = 11.7382 (5)\) Å  

\(\beta = 101.005 (4)^\circ\)  

\(T = 200\) K  

\(\mu = 4.11\) mm\(^{-1}\)  

\(\Delta \rho_{\text{max}} = 0.55\) e Å\(^{-3}\)  

\(\Delta \rho_{\text{min}} = -0.56\) e Å\(^{-3}\)  

Data collection  

Oxford Diffraction Gemini-S CCD detector diffractometer  

Absorption correction: multi-scan  

\(CrysAlis PRO\) (Agilent, 2012)  

3773 measured reflections  

1164 independent reflections  

1118 reflections with \(I > 2\sigma(I)\)  

Refinement  

\(R(F^2) = 0.021\)  

\(wR(F^2) = 0.053\)  

\(S = 0.98\)  

89 parameters  

H-atom parameters constrained  

\(\Delta \rho_{\text{max}} = 0.55\) e Å\(^{-3}\)  

\(\Delta \rho_{\text{min}} = -0.56\) e Å\(^{-3}\)  

Table 1  

Selected bond lengths (Å).  

\[\begin{array}{llll}
\text{Cs1—C15} & 3.7151 (11) & \text{Cs1—O21^iv} & 3.150 (2) \\
\text{Cs1—C16} & 3.6052 (11) & \text{Cs1—O21^vi} & 3.150 (2) \\
\text{Cs1—O1W} & 3.129 (3) & \text{Cs1—Cl3} & 3.7127 (4) \\
\text{Cs1—O21^v} & 3.116 (2) & \text{Cs1—Cl3} & 3.7127 (4) \\
\text{Cs1—O21^vii} & 3.116 (2) & \\
\end{array}\]  

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

Table 2  

Hydrogen-bond geometry (Å, \(^\circ\)).  

\[\begin{array}{llllll}
\text{D—H...A} & \text{D—H} & \text{H...A} & \text{D—A} & \text{D—H...A} \\
\text{O1W—H11W...O21^vii} & 0.92 & 2.00 & 2.905 (3) & 168 \\
\text{N4—H42...N1^viii} & 0.79 & 2.44 & 2.985 (5) & 127 \\
\end{array}\]  

Symmetry codes: (vii) \(-x, -y, -z+1\); (viii) \(x-1, y, z\)  

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, 2012); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.
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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2705).

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Poly[(µ₆-4-amino-3,5,6-trichloropyridine-2-carboxylato)aquacaesium]

Graham Smith

Comment

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 picloramato ligands in the crystallographic literature. Examples include picloram as a bidentate chelate ligand [with Mn⁶⁺ (Smith et al., 1981a) and Cu⁶⁺ (O’Reilly et al., 1983)], while in the Mg complex (Smith et al., 1981b), picloram acts as a counter-anion. A caesium complex derived from dipicolinic acid has also been reported (Santra et al., 2011).

The reaction of picloram with caesium hydroxide in aqueous ethanol gave crystals of the title compound [Cs(C₆H₂Cl₃N₂O₂)(H₂O)]ₙ, and the structure is reported herein. In this structure, the Cs⁺ cation lies on a crystallographic mirror plane which also contains the coordinating monodentate water molecule and all non-H atoms of the picloramate ligand except the carboxyl O-atom donors (Fig. 1). The irregular CsCl₅O₅ coordination sphere comprises chlorine donors from the ortho-related ring substituents (Cl⁵, Cl⁶) in a bidentate chelate mode [Cs—Cl, 3.6052 (11), 3.7151 (11) Å], with the third chlorine (Cl₃) [Cs—Cl, 3.7127 (4) Å] bridging neighbouring Cs⁺ cations [Cs···Cs⁺, Cs···Cs⁺ = 4.9008 (3) Å] [for (x), -x + 1, y - 1/2, -z + 2; for (xi), -x + 1, y + 1/2, -z + 2], as well as a bidentate chelate and bridging carboxyl group. Although in most structures containing caesium and related ligands, the Cl atom is anionic rather than coordinating, an example of a coordinating carbon-bound Cl is known in which 1,2-dichloroethane acts as a bidentate chelate ligand (Levitskaia et al., 2000). The Cs—Cl bond lengths in that structure are shorter than those in the title complex (3.46–3.56 Å).

In the present complex, sheets are formed parallel to (010) (Fig. 2) and these are extended into a three-dimensional coordination polymer structure through the carboxyl group of the picloram ligand which bridges the sheets down [010] (Fig. 3). The amine group gives weak intramolecular N—H···Cl₅ and ···Cl₆ interactions and as well forms inter-complex N—H···Npyridine hydrogen bonds which accompany water O—H···Ocarboxyl hydrogen-bonding interactions in the structure (Table 2).

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 4-amino-3,5,6-trichloropicolinic acid in 20 ml of 10% ethanol–water. Room temperature evaporation of the solution to incipient dryness gave colourless crystal plates of the title complex from which a specimen was cleaved for the X-ray analysis.

Refinement

Hydrogen atoms of the coordinating water molecule and the amine group were located in a difference-Fourier synthesis but were allowed to ride in the refinement with \( U_{eq}(H) = 1.2 U_{eq}(N) \) or \( 1.5 U_{eq}(O) \).
Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); 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).

Figure 1

The molecular configuration and atom-numbering scheme for the title compound, with non-H atoms drawn as 50% probability ellipsoids. For symmetry codes: see Table 1.

Figure 2

The sheet structure viewed perpendicular to the crystallographic mirror planes, with intermolecular hydrogen bonds and intramolecular N—H···Cl associations shown as dashed lines. For symmetry codes, see Fig. 1 and Table 1.
Figure 3
The packing in the unit cell viewed along the mirror planes showing inter-plane carboxyl bridges and hydrogen-bonding associations (Table 2) as dashed lines.

Poly[(μ₆-4-amino-3,5,6-trichloropyridine-2-carboxylato)aquacaesium]

Crystal data
[Cs(C₆H₂Cl₃N₂O₂)(H₂O)]

$M_r = 391.37$
Monoclinic, $P2_1/m$
Hall symbol: -P 2yb
$a = 7.0816 (3)$ Å
$b = 6.6863 (2)$ Å
$c = 11.7382 (5)$ Å
$β = 101.005 (4)^o$
$V = 545.58 (4)$ Å$^3$
$Z = 2$

Data collection
Oxford Diffraction Gemini-S CCD detector
diffraclactor
Radiation source: Enhance Mo X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm$^{-1}$
$ω$ scans

$F(000) = 368$
$D_x = 2.382$ Mg m$^{-3}$
Mo $Kα$ radiation, $λ = 0.71073$ Å
Cell parameters from 3047 reflections
$θ = 3.5–28.7^o$
$μ = 4.11$ mm$^{-1}$
$T = 200$ K
Plate, colourless
$0.25 × 0.20 × 0.08$ mm

Absorption correction: multi-scan
($CrysAlis$ PRO; Agilent, 2012)
$T_{min} = 0.67$, $T_{max} = 0.98$
3773 measured reflections
1164 independent reflections
1118 reflections with $I > 2σ(I)$
$R_{int} = 0.026$
θ_{max} = 26.0°, \theta_{min} = 3.5°  \quad k = -8\rightarrow 8

h = -8\rightarrow 7  \quad l = -11\rightarrow 14

**Refinement**

**Refinement on F^2**

Least-squares matrix: full

\( R(F^2 > 2\sigma(F^2)) = 0.021 \)

\( wR(F^2) = 0.053 \)

\( S = 0.98 \)

1164 reflections

89 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

\( w = 1/\left[ \sigma^2(F_o^2) + (0.0338P)^2 + 0.1378P \right] \)

\( \Delta/\sigma \)max = 0.001

\( \Delta \rho_{max} = 0.55 \text{ e Å}^{-3} \)

\( \Delta \rho_{min} = -0.56 \text{ e Å}^{-3} \)

Extinction correction: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 2012),

\( Fc^* = kFc[1+0.001xFc^2\lambda^3/sin(2\theta)]^{1/4} \)

Extinction coefficient: 0.0132 (11)

**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   | \( U_{iso}^{eq} \) |
|----|-----|-----|-----|---------------------|
| Cs1| 0.29271 (3) | 0.2500 | 0.885412 (19) | 0.02831 (13) |
| Cl3| -0.06235 (13) | 0.2500 | 0.12344 (9) | 0.0326 (2) |
| Cl5| -0.01008 (14) | 0.2500 | 0.58974 (9) | 0.0291 (2) |
| Cl6| 0.44747 (14) | 0.2500 | 0.61009 (9) | 0.0335 (2) |
| O1W| -0.1573 (4) | 0.2500 | 0.8385 (3) | 0.0433 (8) |
| H11W| -0.2387 | 0.1425 | 0.8335 | 0.065* |
| O21| 0.4110 (3) | 0.0836 (3) | 0.14016 (17) | 0.0369 (5) |
| N1| 0.3823 (4) | 0.2500 | 0.3865 (3) | 0.0223 (6) |
| N4| -0.2153 (5) | 0.2500 | 0.3441 (3) | 0.0380 (8) |
| H41| -0.2870 | 0.2500 | 0.2908 | 0.046* |
| H42| -0.2700 | 0.2500 | 0.3968 | 0.046* |
| C2| 0.2692 (5) | 0.2500 | 0.2807 (3) | 0.0211 (7) |
| C3| 0.0719 (5) | 0.2500 | 0.2649 (3) | 0.0230 (7) |
| C4| -0.0239 (5) | 0.2500 | 0.3586 (3) | 0.0241 (8) |
| C5| 0.0961 (5) | 0.2500 | 0.4690 (3) | 0.0224 (7) |
| C6| 0.2937 (5) | 0.2500 | 0.4763 (3) | 0.0221 (7) |
| C21| 0.3725 (5) | 0.2500 | 0.1780 (3) | 0.0253 (8) |

**Atomic displacement parameters (Å²)**

|    | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|----|---------------|---------------|---------------|---------------|---------------|---------------|
| Cs1| 0.02573 (17) | 0.03285 (17) | 0.02648 (18) | 0.000 | 0.00536 (11) | 0.000 |

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|     | 0.0204 (5) | 0.0427 (5) | 0.0316 (5) | 0.000 | −0.0029 (4) | 0.000 |
|-----|-------------|-------------|-------------|-------|-------------|-------|
| Cl5 | 0.0277 (5)  | 0.0283 (5)  | 0.0359 (5)  | 0.000 | 0.0172 (4)  | 0.000 |
| Cl6 | 0.0263 (5)  | 0.0492 (6)  | 0.0243 (5)  | 0.000 | 0.0034 (4)  | 0.000 |
| O1W | 0.0298 (16) | 0.0423 (17) | 0.056 (2)   | 0.000 | 0.0042 (15) | 0.000 |
| O21 | 0.0456 (12) | 0.0340 (11) | 0.0352 (12) | 0.0137 (9) | 0.0178 (10) | 0.0035 (9) |
| N1  | 0.0173 (15) | 0.0238 (15) | 0.0266 (17) | 0.000 | 0.0061 (12) | 0.000 |
| N4  | 0.0158 (16) | 0.058 (2)   | 0.041 (2)   | 0.000 | 0.0076 (14) | 0.000 |
| C2  | 0.0187 (17) | 0.0181 (16) | 0.027 (2)   | 0.000 | 0.0048 (14) | 0.000 |
| C3  | 0.0169 (17) | 0.0240 (17) | 0.027 (2)   | 0.000 | 0.0008 (15) | 0.000 |
| C4  | 0.0164 (17) | 0.0187 (16) | 0.037 (2)   | 0.000 | 0.0052 (15) | 0.000 |
| C5  | 0.0198 (17) | 0.0196 (16) | 0.030 (2)   | 0.000 | 0.0116 (15) | 0.000 |
| C6  | 0.0194 (17) | 0.0216 (16) | 0.0243 (19) | 0.000 | 0.0020 (14) | 0.000 |
| C21 | 0.0149 (16) | 0.036 (2)   | 0.0238 (19) | 0.000 | 0.0002 (14) | 0.000 |

Geometric parameters (Å, °)

|          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|
| Cs1—Cl5  | 3.7151 (11) | O1W—H11W | 0.9200   |          |          |          |
| Cs1—Cl6  | 3.6052 (11) | O1W—H11W v   | 0.9200   |          |          |          |
| Cs1—O1W  | 3.129 (3)   | N1—C2     | 1.343 (5) |          |          |          |
| Cs1—O21i | 3.116 (2)   | N1—C6     | 1.326 (5) |          |          |          |
| Cs1—O21ii| 3.116 (2)   | N4—C4     | 1.333 (5) |          |          |          |
| Cs1—O21iii| 3.150 (2)  | N4—H42    | 0.7900   |          |          |          |
| Cs1—O21iv| 3.150 (2)   | N4—H41    | 0.7300   |          |          |          |
| Cs1—Cl3v| 3.7127 (4)  | C2—C3     | 1.374 (5) |          |          |          |
| Cs1—Cl3vi| 3.7127 (4)  | C2—C21    | 1.525 (5) |          |          |          |
| Cl5—C5   | 1.727 (4)   | C3—C4     | 1.398 (5) |          |          |          |
| Cl6—C6   | 1.732 (4)   | C3—Cl3    | 1.749 (4) |          |          |          |
| C21—O21  | 1.247 (3)   | C4—C5     | 1.408 (5) |          |          |          |
| C21—O21i | 1.247 (3)   | C5—C6     | 1.386 (5) |          |          |          |

|          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|
| Cl5—Cs1—Cl6 | 51.87 (2) | Cl3v—Cs1—O21iii | 75.19 (4) |          |          |          |
| Cl5—Cs1—O1W | 56.55 (7) | O21i—Cs1—O21ii | 91.43 (5) |          |          |          |
| Cl5—Cs1—O21v | 152.65 (4) | O21i—Cs1—O21iii | 77.10 (5) |          |          |          |
| Cl3v—Cs1—Cl5 | 78.56 (2) | O21i—Cs1—O21ii | 106.40 (5) |          |          |          |
| Cl3vi—Cs1—Cl5 | 78.56 (2) | Cs1—Cl3—C3 | 100.54 (5) |          |          |          |
| Cl5—Cs1—O21i | 100.91 (4) | Cs1—Cl3—C3 | 100.54 (5) |          |          |          |
| Cl5—Cs1—O21ii| 100.91 (4) | Cs1—Cl3—C3 | 128.44 (3) |          |          |          |
| Cl5—Cs1—O21iii| 152.65 (4) | Cs1—Cl5—C5 | 120.18 (13) |          |          |          |
| Cl6—Cs1—O1W | 108.42 (7) | Cs1—Cl6—C6 | 124.53 (13) |          |          |          |
| Cl6—Cs1—O21ix | 141.22 (4) | Cs1—O1W—H11W | 128.00 |          |          |          |
| Cl3v—Cs1—Cl6 | 100.49 (2) | Cs1—O1W—H11W viii | 128.00 |          |          |          |
| Cl6—Cs1—O21i | 65.68 (4) | H11W—O1W—H11W viii | 103.00 |          |          |          |
| Cl6—Cs1—O21ii| 65.68 (4) | C2—N1—C6 | 116.5 (3) |          |          |          |
| Cl6—Cs1—O21iii| 141.22 (4) | C4—N4—H41 | 130.00 |          |          |          |
| O1W—Cs1—O21iv | 104.15 (7) | H41—N4—H42 | 108.00 |          |          |          |

**Geometric parameters (Å, °)**

|          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|
|          |          |          |          |          |          |          |
|          |          |          |          |          |          |          |
|          |          |          |          |          |          |          |
|          |          |          |          |          |          |          |
|          |          |          |          |          |          |          |
|          |          |          |          |          |          |          |
|          |          |          |          |          |          |          |
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\[
\begin{align*}
O1W—Cs1—O21^{iii} & \quad 104.15 (7) \quad C2—C3—C4 & \quad 121.8 (3) \\
Cl3^{v}—Cs1—O21^{iv} & \quad 75.19 (4) \quad Cl3—C3—C2 & \quad 118.9 (3) \\
Cl3^{vi}—Cs1—O21^{iv} & \quad 112.36 (4) \quad Cl3—C3—C4 & \quad 119.3 (3) \\
O21^{iv}—Cs1—O21^{i} & \quad 106.40 (5) \quad N4—C4—C5 & \quad 122.5 (3) \\
O21^{iv}—Cs1—O21^{a} & \quad 77.10 (5) \quad C3—C4—C5 & \quad 115.2 (3) \\
O21^{iv}—Cs1—O21^{i} & \quad 41.36 (5) \quad Cl3—C3—C4 & \quad 122.3 (3) \\
O21^{v}—Cs1—O21^{i} & \quad 128.44 (2) \quad C4—C5—C6 & \quad 118.8 (3) \\
Cl3^{v}—Cs1—O21^{i} & \quad 160.44 (4) \quad Cl5—C5—C6 & \quad 118.4 (3) \\
Cl3^{v}—Cs1—O21^{i} & \quad 69.70 (4) \quad Cl5—C6—C5 & \quad 118.4 (3) \\
Cl3^{v}—Cs1—O21^{i} & \quad 112.36 (4) \quad Cl5—C5—C6 & \quad 118.4 (3) \\
O1W—Cs1—Cl5—C5 & \quad 180.00 (1) \quad C21—C2—C3—C4 & \quad 180.00 (1) \\
O1W—Cs1—Cl5—C5 & \quad 180.00 (1) \quad Cl2—C2—C3—C4 & \quad 180.00 (1) \\
Cl5—Cs1—Cl6—C6 & \quad 0.00 (1) \quad Cl3—C3—C4—N4 & \quad 0.00 (1) \\
Cs1—Cl5—C5—C4 & \quad 180.00 (1) \quad Cl3—C3—C4—C5 & \quad 180.00 (1) \\
Cl5—Cs1—Cl6—C6 & \quad 0.00 (1) \quad Cl3—C3—C4—C5 & \quad 180.00 (1) \\
Cs1—Cl6—C6—C5 & \quad 0.00 (1) \quad Cl3—C3—C4—C5 & \quad 180.00 (1) \\
C6—N1—C2—C3 & \quad 0.00 (1) \quad N4—C4—C5—Cl5 & \quad 180.00 (1) \\
C6—N1—C2—C3 & \quad 0.00 (1) \quad N4—C4—C5—Cl5 & \quad 180.00 (1) \\
C2—N1—C6—C5 & \quad 0.00 (1) \quad C3—C4—C5—Cl5 & \quad 180.00 (1) \\
C2—N1—C6—C5 & \quad 0.00 (1) \quad C3—C4—C5—Cl5 & \quad 180.00 (1) \\
N1—C2—C3—Cl3 & \quad 0.00 (1) \quad C3—C4—C5—Cl5 & \quad 180.00 (1) \\
N1—C2—C3—Cl3 & \quad 0.00 (1) \quad C3—C4—C5—Cl5 & \quad 180.00 (1) \\
C21—C2—C3—Cl3 & \quad 0.00 (1) \quad C4—C5—C6—N1 & \quad 180.00 (1) \\
C21—C2—C3—Cl3 & \quad 0.00 (1) \quad C4—C5—C6—N1 & \quad 180.00 (1) \\
\end{align*}
\]

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

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| O1W—H11W···O21^x | 0.92 | 2.00 | 2.905 (3) | 168 |
| N4—H42···N1^xi | 0.79 | 2.44 | 2.985 (5) | 127 |
| N4—H42···Cl5 | 0.79 | 2.63 | 2.971 (4) | 108 |
| N4—H41···Cl3 | 0.73 | 2.75 | 2.992 (4) | 102 |

Symmetry codes: (x) \(-x, -y, -z+1\); (xi) \(x-1, y, z\).