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# 3-Chloro-2-methylanilinium chloride monohydrate

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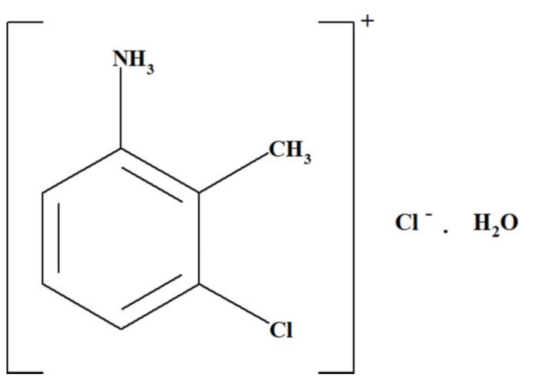
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.055; $wR$ factor = 0.163; data-to-parameter ratio = 39.5.

In the title hydrated salt, $C_7H_9ClN^+\cdot Cl^-\cdot H_2O$, the organic cations, anions and water molecules are connected by N—H···Cl, N—H···O and O—H···Cl hydrogen bonds. These interactions lead to the formation of layers parallel to the *ac* plane.

## Related literature

For hydrogen bonds, see: Steiner (2002); Jayaraman *et al.* (2002). For the crystal structure of a related protonated amine, see: Hamdi *et al.* (2014). For related structures containing the 3-chloro-2-methylanilinium cation, see: Khemiri *et al.* (2008); Bel Haj Salah *et al.* (2014). For geometrical features, see: Oueslati *et al.* (2005).




## Experimental

*Crystal data*

$C_7H_9ClN^+\cdot Cl^-\cdot H_2O$
$M_r$ = 196.07
Orthorhombic, $P2_12_12_1$
$a$ = 7.434 (4) Å
$b$ = 7.475 (3) Å
$c$ = 16.785 (2) Å
$V$ = 932.7 (6) Å$^3$
$Z$ = 4
Ag $K\alpha$ radiation
$\lambda$ = 0.56087 Å
$\mu$ = 0.33 mm$^{-1}$
$T$ = 293 K
0.50 × 0.25 × 0.15 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
5019 measured reflections
3947 independent reflections
1804 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.035
2 standard reflections every 120 min intensity decay: 6%

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.163
$S$ = 0.92
3947 reflections
100 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.35 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.42 e Å$^{-3}$
Absolute structure: Flack (1983), unique data only
Absolute structure parameter: −0.04 (19)

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$W$—H1$W$1···Cl2$^{\rm i}$ | 0.86 | 2.28 | 3.129 (3) | 169 |
| O1$W$—H2$W$1···Cl2 | 0.86 | 2.36 | 3.139 (3) | 151 |
| N1—H1$A$···Cl2$^{\rm ii}$ | 0.89 | 2.70 | 3.178 (3) | 115 |
| N1—H1$A$···O1$W^{\rm iii}$ | 0.89 | 2.30 | 2.667 (4) | 105 |
| N1—H1$B$···Cl2$^{\rm iv}$ | 0.89 | 2.68 | 3.187 (3) | 117 |
| N1—H1$B$···O1$W^{\rm iii}$ | 0.89 | 2.28 | 2.667 (4) | 106 |
| N1—H1$C$···Cl2$^{\rm ii}$ | 0.89 | 2.83 | 3.178 (3) | 105 |

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Supporting information for this paper is available from the IUCr electronic archives (Reference: FJ2671).

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# supporting information

*Acta Cryst.* (2014). E**70**, o643 [doi:10.1107/S1600536814009921]

## 3-Chloro-2-methylanilinium chloride monohydrate

**Arbi Maroua, Khederi Lamia, Hamdi Ahmed and Rzaigui Mohamed**

### S1. Comment

Hydrogen bonding is of interest because of their prevalent occurrence in biological systems (Steiner 2002; Jayaraman *et al.*, 2002). Therefore, it is extremely useful to search simple molecules allowing understanding the configuration and the function of some complex macromolecules. The title compound, was prepared as part of our ongoing studies of hydrogen-bonding interactions in the crystal structure of protonated amines (Hamdi *et al.*, 2014). Structures containing the 3-chloro-2-methylanilinium cation have been already reported with dihydrogenphosphate (Khemiri *et al.*, 2008) and cyclohexaphosphate (Bel Haj Salah *et al.*, 2014).

The asymmetric unit of the title compound (I), illustrated in Fig. 1, consists of one organic cation, one $Cl^-$ anion and one water molecule. All bond distances and angles are within the ranges of accepted values. Moreover, they are close to respect the geometrical features observed in the crystal structure of 5-chloro-2-methylanilinium chloride (Oueslati *et al.*, 2005). Components of the asymmetric unit develop different H-bonds, N—H···Cl, N—H···OW and OW—H···Cl (Fig. 2) that keep them in a state where the aromatic rings of organic buildings are oriented in the direction of the *bc* planes to form centro-symmetric pairs interconnected by hydrogen bonds in the direction of the *b* axis (Fig. 2). The resulting sequences are alternated to form the crystal packing of the title compound (Fig. 3).

### S2. Experimental

An aqueous solution of $AlCl_3$ (1 mmol) and 3-chloro-2-methylaniline (2 mmol) in hydrochloric acid was stirred for several minutes at room temperature and slowly evaporated to dryness for two weeks. White single crystals of the title compound were carefully isolated under polarizing microscope for X-ray diffraction analysis.

### S3. Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances of 0.93 Å for phenyl and 0.96 Å for methyl groups, and N—H = 0.89 Å; $U_{iso}$ (H) = 1.2 $U_{iso}$ (C,*N*) for phenyl and ammonium H atoms and 1.5 $U_{iso}$ (C) for methyl. In water molecule the O—H distances were restrained to 0.85 (1) Å, and the distance H···H to 1.44 (2) Å.

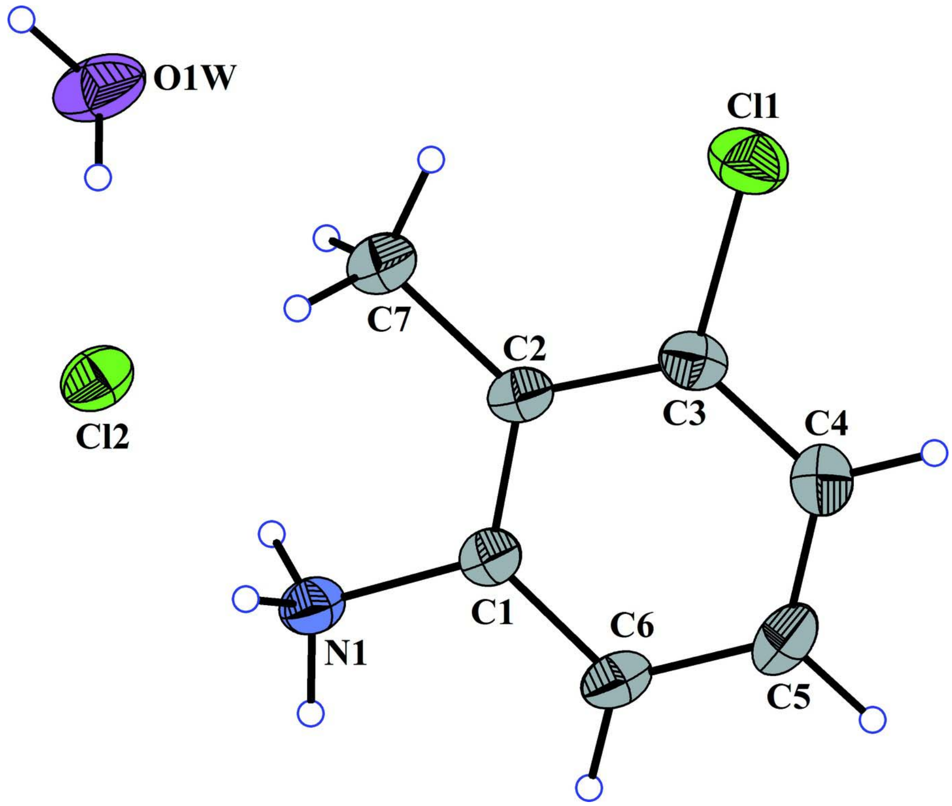


**Figure 1**

*ORTEP* drawing of the asymmetric unit of title compound with displacement ellipsoids drawn at 40% probability level. [Symmetry code: (i) *x*, *y*, *z*]

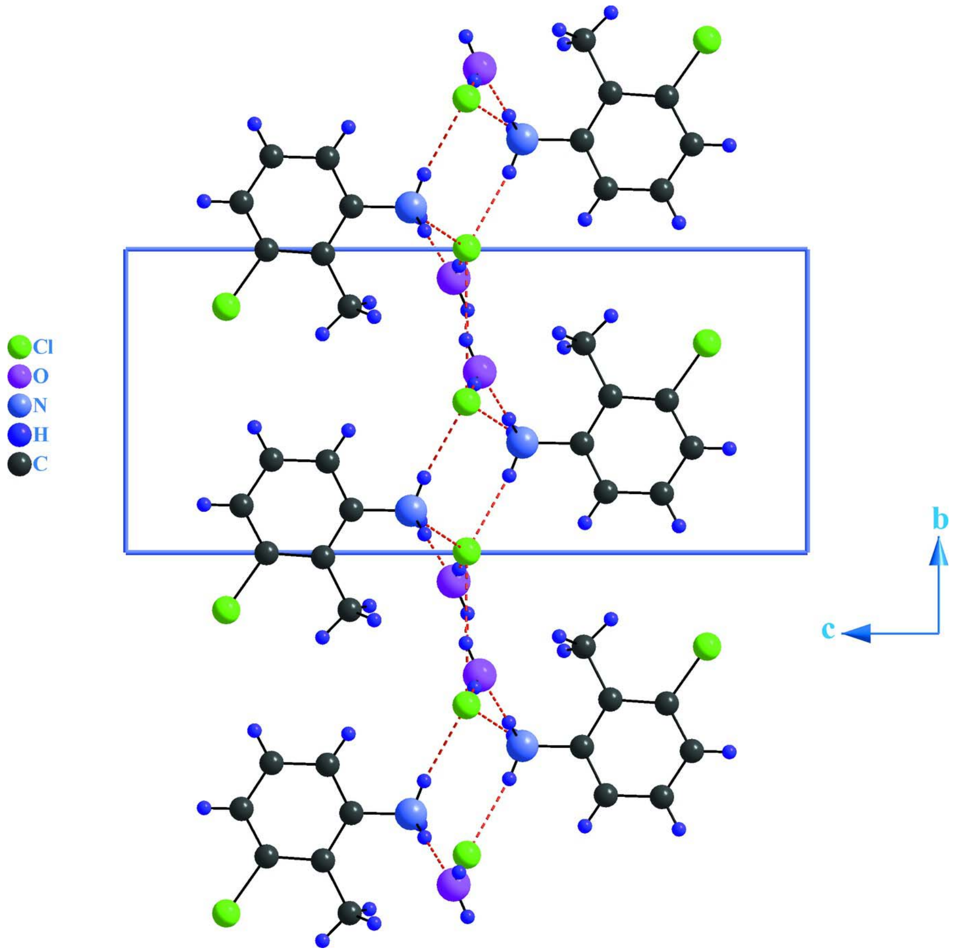


**Figure 2**

A view of the atomic arrangement of the title compound along the *a* axis with H bonds shown as dashed lines.

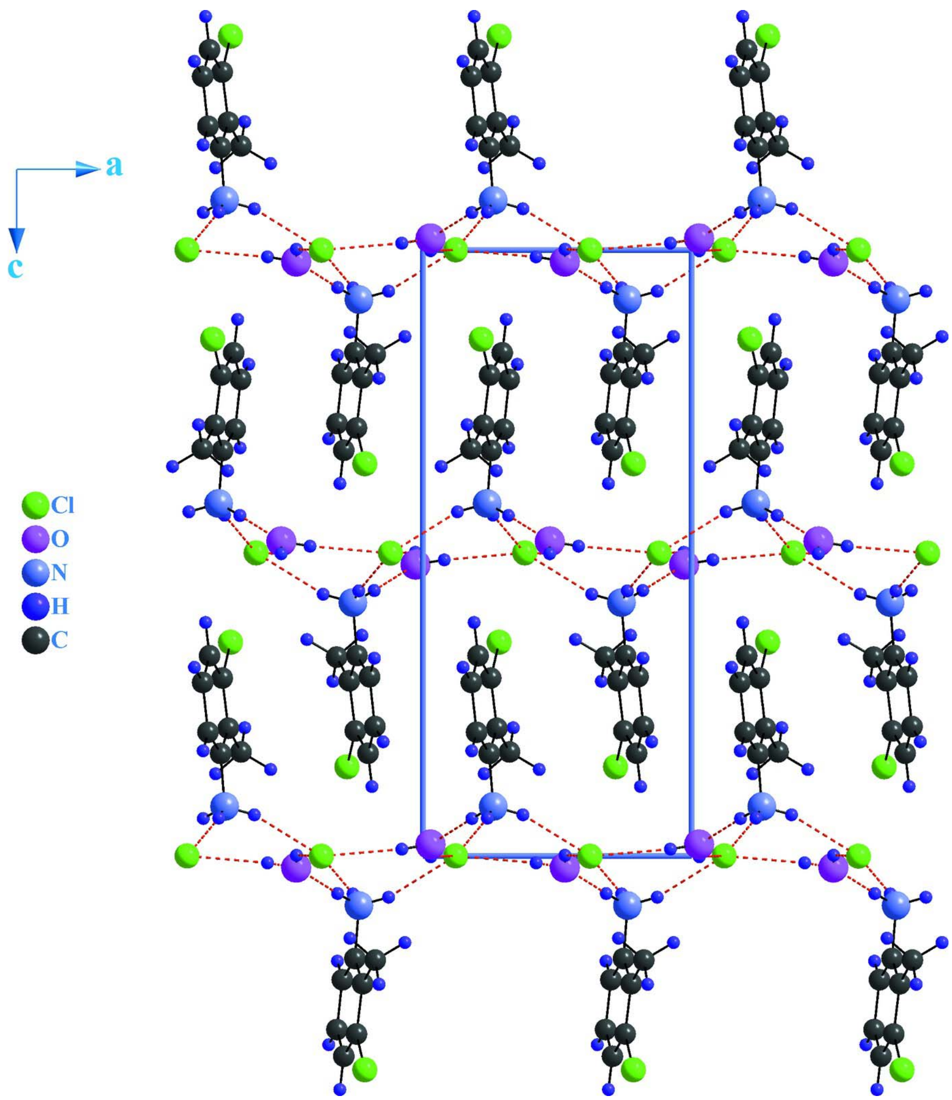


**Figure 3**

A diagram of the crystal packing in the title compound, viewed down the *b* axis.

**3-Chloro-2-methylanilinium chloride monohydrate**

*Crystal data*

| | |
|---|---|
| $C_7H_9ClN^+\cdot Cl^-\cdot H_2O$ | $F(000) = 408$ |
| $M_r = 196.07$ | $D_x = 1.396$ Mg m$^{-3}$ |
| Orthorhombic, $P2_12_12_1$ | Ag $K\alpha$ radiation, $\lambda = 0.56087$ Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 25 reflections |
| $a = 7.434$ (4) Å | $\theta = 9$–$11°$ |
| $b = 7.475$ (3) Å | $\mu = 0.33$ mm$^{-1}$ |
| $c = 16.785$ (2) Å | $T = 293$ K |
| $V = 932.7$ (6) Å$^3$ | Rectangular, colorless |
| $Z = 4$ | $0.50 \times 0.25 \times 0.15$ mm |

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
non–profiled $\omega$ scans
5019 measured reflections
3947 independent reflections
1804 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.4°$
$h = -3 \rightarrow 12$
$k = -3 \rightarrow 12$
$l = -2 \rightarrow 28$
2 standard reflections every 120 min
intensity decay: 6%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.163$
$S = 0.92$
3947 reflections
100 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.0841P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å$^{-3}$
$\Delta\rho_{min} = -0.42$ e Å$^{-3}$
Absolute structure: Flack (1983), unique data only
Absolute structure parameter: −0.04 (19)

*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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.21684 (13) | 0.68978 (12) | 0.14721 (5) | 0.0605 (3) |
| N1 | 0.2400 (3) | 0.3630 (3) | 0.41835 (13) | 0.0397 (7) |
| C1 | 0.2542 (4) | 0.3587 (4) | 0.33084 (16) | 0.0375 (8) |
| C2 | 0.2248 (4) | 0.5163 (4) | 0.28915 (15) | 0.0368 (7) |
| C3 | 0.2477 (4) | 0.5022 (5) | 0.20642 (15) | 0.0429 (8) |
| C4 | 0.2959 (5) | 0.3453 (4) | 0.16946 (19) | 0.0520 (10) |
| C5 | 0.3203 (5) | 0.1946 (5) | 0.2135 (2) | 0.0581 (10) |
| C6 | 0.3010 (4) | 0.2003 (4) | 0.29557 (18) | 0.0435 (8) |
| C7 | 0.1793 (5) | 0.6906 (4) | 0.3283 (2) | 0.0551 (10) |
| O1W | 0.5280 (3) | 0.0960 (3) | 0.01902 (16) | 0.0676 (9) |
| Cl2 | 0.62142 (10) | 0.50337 (10) | 0.00015 (4) | 0.0469 (2) |
| H1A | 0.20910 | 0.47250 | 0.43403 | 0.0477* |
| H1B | 0.34559 | 0.33388 | 0.43972 | 0.0477* |
| H1C | 0.15674 | 0.28516 | 0.43419 | 0.0477* |
| H3 | 0.31954 | 0.09820 | 0.32617 | 0.0522* |

| | | | | |
|---|---|---|---|---|
| H4 | 0.35005 | 0.08749 | 0.18857 | 0.0698* |
| H5 | 0.31181 | 0.34223 | 0.11452 | 0.0624* |
| H7A | 0.16524 | 0.78143 | 0.28835 | 0.0825* |
| H7B | 0.27430 | 0.72387 | 0.36406 | 0.0825* |
| H7C | 0.06902 | 0.67814 | 0.35757 | 0.0825* |
| H1W1 | 0.42091 | 0.05452 | 0.01130 | 0.0825* |
| H2W1 | 0.52857 | 0.20105 | −0.00122 | 0.0825* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0707 (6) | 0.0555 (5) | 0.0553 (4) | 0.0060 (5) | −0.0007 (4) | 0.0165 (4) |
| N1 | 0.0420 (14) | 0.0319 (11) | 0.0452 (11) | 0.0055 (11) | 0.0059 (11) | 0.0037 (9) |
| C1 | 0.0382 (16) | 0.0326 (12) | 0.0417 (12) | 0.0018 (12) | 0.0008 (12) | −0.0010 (10) |
| C2 | 0.0342 (13) | 0.0304 (12) | 0.0458 (13) | 0.0014 (13) | −0.0018 (12) | −0.0004 (11) |
| C3 | 0.0385 (16) | 0.0449 (14) | 0.0452 (13) | 0.0025 (16) | 0.0000 (12) | 0.0064 (14) |
| C4 | 0.0593 (19) | 0.0548 (19) | 0.0419 (14) | 0.006 (2) | 0.0005 (15) | −0.0039 (14) |
| C5 | 0.074 (2) | 0.0428 (16) | 0.0576 (18) | 0.012 (2) | 0.0078 (18) | −0.0144 (16) |
| C6 | 0.0456 (16) | 0.0296 (12) | 0.0554 (15) | 0.0057 (15) | 0.0021 (14) | −0.0023 (13) |
| C7 | 0.073 (2) | 0.0393 (16) | 0.0529 (16) | 0.0120 (19) | 0.0011 (16) | −0.0014 (16) |
| O1W | 0.0608 (15) | 0.0390 (12) | 0.103 (2) | −0.0020 (11) | −0.0192 (16) | 0.0113 (13) |
| Cl2 | 0.0476 (3) | 0.0359 (3) | 0.0573 (4) | −0.0004 (3) | −0.0068 (4) | 0.0006 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C3 | 1.734 (4) | C2—C3 | 1.403 (4) |
| O1W—H2W1 | 0.8600 | C3—C4 | 1.374 (5) |
| O1W—H1W1 | 0.8600 | C4—C5 | 1.360 (5) |
| N1—C1 | 1.473 (4) | C5—C6 | 1.386 (5) |
| N1—H1A | 0.8900 | C4—H5 | 0.9300 |
| N1—H1C | 0.8900 | C5—H4 | 0.9300 |
| N1—H1B | 0.8900 | C6—H3 | 0.9300 |
| C1—C2 | 1.388 (4) | C7—H7C | 0.9600 |
| C1—C6 | 1.369 (4) | C7—H7A | 0.9600 |
| C2—C7 | 1.498 (4) | C7—H7B | 0.9600 |
| | | | |
| H1W1—O1W—H2W1 | 106.00 | C3—C4—C5 | 119.8 (3) |
| H1A—N1—H1C | 109.00 | C4—C5—C6 | 120.1 (3) |
| H1B—N1—H1C | 109.00 | C1—C6—C5 | 118.9 (3) |
| C1—N1—H1B | 109.00 | C3—C4—H5 | 120.00 |
| C1—N1—H1C | 109.00 | C5—C4—H5 | 120.00 |
| C1—N1—H1A | 109.00 | C6—C5—H4 | 120.00 |
| H1A—N1—H1B | 109.00 | C4—C5—H4 | 120.00 |
| C2—C1—C6 | 123.8 (3) | C1—C6—H3 | 121.00 |
| N1—C1—C2 | 118.2 (2) | C5—C6—H3 | 121.00 |
| N1—C1—C6 | 117.9 (3) | C2—C7—H7B | 109.00 |
| C1—C2—C7 | 123.6 (2) | C2—C7—H7C | 109.00 |
| C3—C2—C7 | 121.8 (3) | C2—C7—H7A | 109.00 |

| | | | |
|---|---|---|---|
| C1—C2—C3 | 114.6 (3) | H7A—C7—H7C | 109.00 |
| Cl1—C3—C4 | 117.8 (2) | H7B—C7—H7C | 109.00 |
| C2—C3—C4 | 122.9 (3) | H7A—C7—H7B | 109.00 |
| Cl1—C3—C2 | 119.4 (3) | | |
| | | | |
| N1—C1—C2—C3 | 177.7 (3) | C1—C2—C3—C4 | −0.2 (5) |
| N1—C1—C2—C7 | 0.2 (4) | C7—C2—C3—Cl1 | −1.8 (4) |
| C6—C1—C2—C3 | −0.3 (4) | C7—C2—C3—C4 | 177.6 (3) |
| C6—C1—C2—C7 | −178.0 (3) | Cl1—C3—C4—C5 | −179.5 (3) |
| N1—C1—C6—C5 | −178.1 (3) | C2—C3—C4—C5 | 1.2 (5) |
| C2—C1—C6—C5 | −0.2 (5) | C3—C4—C5—C6 | −1.6 (5) |
| C1—C2—C3—Cl1 | −179.5 (2) | C4—C5—C6—C1 | 1.1 (5) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*W*1···Cl2$^{i}$ | 0.8600 | 2.2800 | 3.129 (3) | 169.00 |
| O1*W*—H2*W*1···Cl2 | 0.8600 | 2.3600 | 3.139 (3) | 151.00 |
| N1—H1*A*···Cl2$^{ii}$ | 0.8900 | 2.7000 | 3.178 (3) | 115.00 |
| N1—H1*A*···O1*W*$^{iii}$ | 0.8900 | 2.3000 | 2.667 (4) | 105.00 |
| N1—H1*B*···Cl2$^{iv}$ | 0.8900 | 2.6800 | 3.187 (3) | 117.00 |
| N1—H1*B*···O1*W*$^{iii}$ | 0.8900 | 2.2800 | 2.667 (4) | 106.00 |
| N1—H1*C*···Cl2$^{ii}$ | 0.8900 | 2.8300 | 3.178 (3) | 105.00 |
| C7—H7*A*···Cl1 | 0.9600 | 2.5000 | 3.053 (4) | 117.00 |

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