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# 2-[Bis(5-chloro-2-pyridylamino)methyl]-pyridine monohydrate

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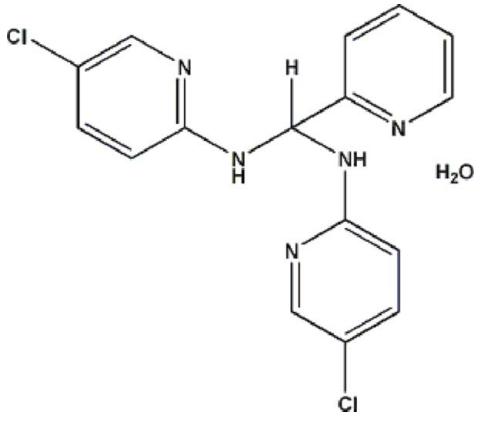
Key indicators: single-crystal X-ray study; $T$ = 150 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.039; $wR$ factor = 0.101; data-to-parameter ratio = 17.4.

In the title compound, the dihedral angles between the 2-amino-5-chloropyridyl rings and the pyridine ring are 56.26 (6)° and 78.83 (5)°; the angle between the 2-amino-5-chloropyridyl rings is 72.42 (5)°. The solvent water molecules are linked to the organic compound by N—H···O, O—H···O, N—H···N and O—H···N hydrogen bonds. $\pi\cdots\pi$ Stacking interactions are also observed between the 2-amino-5-chloropyridyl rings (centroid···centroid distance = 3.243 Å).

## Related literature

For related crystallographic studies, see: Makowska-Grzyska *et al.* (2003); Li *et al.* (2008); Peori *et al.* (2008).




## Experimental

### Crystal data

$C_{16}H_{13}Cl_2N_5\cdot H_2O$
$M_r$ = 364.23
Monoclinic, $C2/c$
$a$ = 34.414 (3) Å
$b$ = 4.4337 (3) Å
$c$ = 26.236 (2) Å
$\beta$ = 124.778 (1)°
$V$ = 3288.0 (4) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.41 mm$^{-1}$
$T$ = 150 (2) K
0.35 × 0.10 × 0.05 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min}$ = 0.870, $T_{max}$ = 0.980
14914 measured reflections
3778 independent reflections
2830 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.042

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.101
$S$ = 1.04
3778 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.25 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$N$···N5$^{i}$ | 0.87 | 2.15 | 2.994 (2) | 165 |
| N4—H4$N$···O1$^{ii}$ | 0.87 | 2.18 | 2.993 (2) | 156 |
| O1—H1$O$···N1 | 0.82 | 1.98 | 2.773 (2) | 164 |
| O1—H2$O$···O1$^{iii}$ | 0.82 | 1.96 | 2.758 (2) | 163 |

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We are grateful to the Research Council of Sharif University of Technology, and Loughborough University for their financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2287).

## References

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

*Acta Cryst.* (2008). E**64**, o2428 [doi:10.1107/S1600536808035940]

## 2-[Bis(5-chloro-2-pyridylamino)methyl]pyridine monohydrate

**Davar M. Boghaei, Mohammad Mahdi Najafpour and Vickie McKee**

### S1. Comment

Primary amines add to imines to form aminal compounds; these are not stable (Peori *et al.*, 2008). The title compound, $C_{16}H_{13}Cl_2N_5.H_2O$, was synthesized by the reaction of 2-amino-5-chloropyridine with 2-pyridinecarbaldehyde in ethanol. Tris(pyridyl)amines are very common ligands and many complexes containing such ligands have been reported (Makowska-Grzyska *et al.*, 2003; Li *et al.*, 2008).

In the title compound, intermolecular N—H···O and N—H···N hydrogen bonds involving amine NH and pyridyl groups form a two dimensional network (Table 1 and Fig. 3). $\pi$–$\pi$ stacking interactions are also observed between the 2-amino-5-chloropyridyl rings [centroid···centroid distance = 3.243 Å]. The dihedral angles between the 2-amino-5-chloropyridyl rings and the pyridine ring are 56.26 (6)° and 78.83 (5)°; the angle between the 2-amino-5-chloropyridyl rings is 72.42 (5)°.

### S2. Experimental

The title compound was synthesized by adding 2-pyridinecarbaldehyde (1 mmol, 107 mg) to a solution of 2-amino-5-chloropyridine (3 mmol, 386 mg) and manganese acetate (0.02 mmol, 4.90 mg) in ethanol (20 ml). The mixture was refluxed with stirring for 7 h. The resultant yellow solution was filtered. Colourless single crystals of the title compound suitable for *X*-ray structure determination were recrystallized from a mixture of ethanol / water (5/1) by slow evaporation of the solvents at room temperature over several days.

### S3. Refinement

The H atoms bonded to C atoms were positioned geometrically and refined using the riding model with $U_{iso}$(H) = 1.2$U_{eq}$(parent atom); C—H = 0.95 and 1.00 Å for aromatic and methine C atoms, respectively. The H atoms bonded to N and O atoms were found in the difference Fourier map and refined with the following *DFIX* restraints: 0.87 (2) Å for N—H and 0.82 (2) Å for O—H. In the final refinement stages the AFIX3 constraint was used for these H atoms.

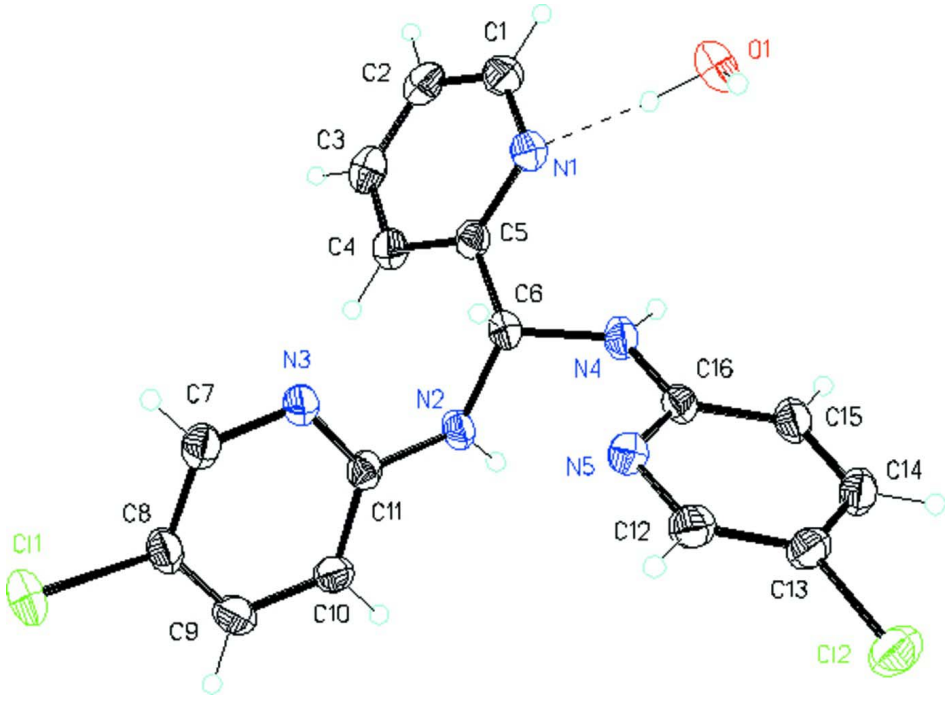


**Figure 1**

View of the molecular structure of the title compound, with displacement ellipsoids for non-H atoms drawn at the 50% probability level. The hydrogen atoms are represented by spheres of arbitrary radius. The hydrogen bond is shown as a dashed line.

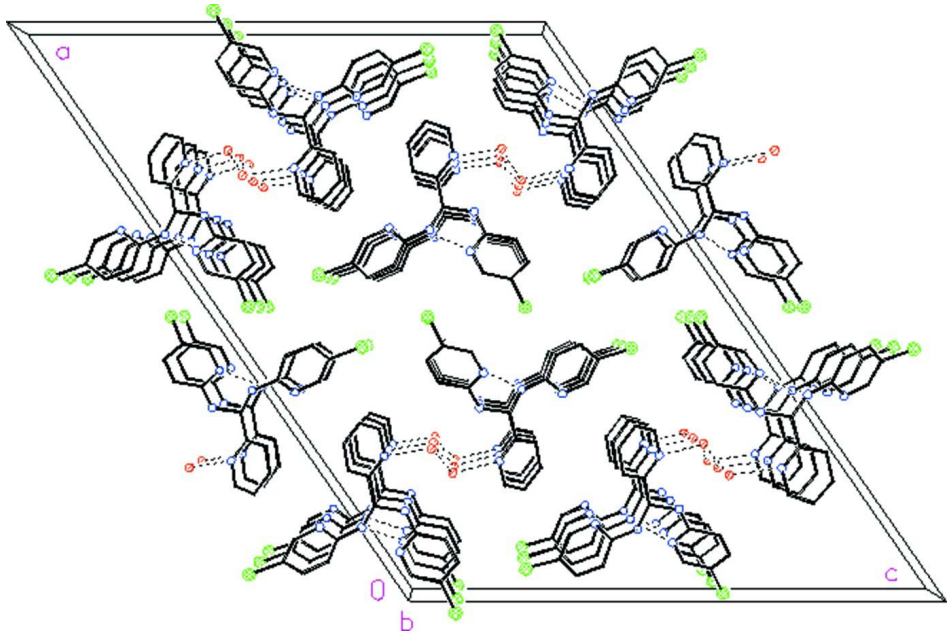


**Figure 2**

View of the crystal structure packing scheme. The dashed lines indicate hydrogen bonds. H atoms have been omitted.

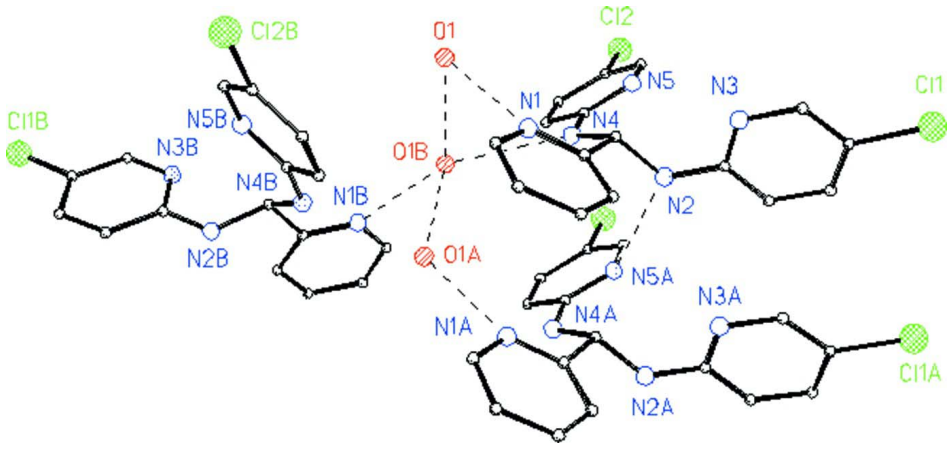


**Figure 3**

View of the hydrogen bonding (dashed lines) scheme. H atoms have been omitted.

### 2-[Bis(5-chloro-2-pyridylamino)methyl]pyridine monohydrate

*Crystal data*

$C_{16}H_{13}Cl_2N_5{\cdot}H_2O$
$M_r = 364.23$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 34.414\ (3)$ Å
$b = 4.4337\ (3)$ Å
$c = 26.236\ (2)$ Å
$\beta = 124.778\ (1)°$
$V = 3288.0\ (4)$ Å$^3$
$Z = 8$
$F(000) = 1504$
$D_x = 1.472$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2781 reflections
$\theta = 2.4–26.1°$
$\mu = 0.41$ mm$^{-1}$
$T = 150$ K
Lath, colourless
0.35 × 0.10 × 0.05 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.870$, $T_{max} = 0.980$
14914 measured reflections
3778 independent reflections
2830 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$
$h = -44\rightarrow44$
$k = -5\rightarrow5$
$l = -34\rightarrow34$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.101$
$S = 1.04$
3778 reflections
217 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
$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 1.3212P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.25729 (5) | 0.5318 (4) | 0.15040 (7) | 0.0272 (3) |
| C1 | 0.30054 (7) | 0.4226 (5) | 0.17347 (9) | 0.0308 (4) |
| H1 | 0.3259 | 0.4888 | 0.2134 | 0.037* |
| C2 | 0.31028 (7) | 0.2185 (4) | 0.14231 (9) | 0.0317 (4) |
| H2 | 0.3414 | 0.1436 | 0.1606 | 0.038* |
| C3 | 0.27344 (7) | 0.1266 (5) | 0.08383 (9) | 0.0330 (4) |
| H3 | 0.2789 | −0.0104 | 0.0607 | 0.040* |
| C4 | 0.22844 (7) | 0.2366 (4) | 0.05934 (9) | 0.0279 (4) |
| H4 | 0.2026 | 0.1759 | 0.0192 | 0.033* |
| C5 | 0.22143 (6) | 0.4366 (4) | 0.09407 (8) | 0.0232 (4) |
| C6 | 0.17286 (6) | 0.5693 (4) | 0.06964 (8) | 0.0235 (4) |
| H6 | 0.1720 | 0.7800 | 0.0554 | 0.028* |
| N2 | 0.13502 (5) | 0.4001 (4) | 0.01720 (6) | 0.0244 (3) |
| H2N | 0.1224 | 0.2485 | 0.0239 | 0.029* |
| N3 | 0.13945 (5) | 0.6845 (3) | −0.05317 (7) | 0.0254 (3) |
| C7 | 0.12129 (7) | 0.7555 (4) | −0.11245 (9) | 0.0279 (4) |
| H7 | 0.1368 | 0.9051 | −0.1206 | 0.033* |
| C8 | 0.08131 (6) | 0.6224 (5) | −0.16202 (8) | 0.0286 (4) |
| Cl1 | 0.06183 (2) | 0.72387 (14) | −0.23748 (2) | 0.04370 (16) |
| C9 | 0.05738 (6) | 0.4096 (5) | −0.15136 (8) | 0.0296 (4) |
| H9 | 0.0295 | 0.3165 | −0.1850 | 0.035* |
| C10 | 0.07470 (6) | 0.3361 (4) | −0.09131 (8) | 0.0255 (4) |
| H10 | 0.0588 | 0.1919 | −0.0825 | 0.031* |
| C11 | 0.11634 (6) | 0.4768 (4) | −0.04267 (8) | 0.0224 (4) |
| N4 | 0.16586 (5) | 0.5834 (4) | 0.11881 (7) | 0.0273 (4) |
| H4N | 0.1839 | 0.4738 | 0.1518 | 0.033* |
| N5 | 0.10283 (5) | 0.9191 (4) | 0.06534 (7) | 0.0267 (3) |
| C12 | 0.06679 (6) | 1.0659 (4) | 0.06110 (9) | 0.0288 (4) |
| H12 | 0.0479 | 1.1975 | 0.0269 | 0.035* |
| C13 | 0.05617 (6) | 1.0341 (4) | 0.10388 (9) | 0.0275 (4) |
| Cl2 | 0.008985 (17) | 1.23175 (12) | 0.09516 (3) | 0.03644 (14) |
| C14 | 0.08384 (7) | 0.8454 (5) | 0.15457 (9) | 0.0298 (4) |
| H14 | 0.0773 | 0.8215 | 0.1849 | 0.036* |
| C15 | 0.12065 (7) | 0.6949 (4) | 0.16002 (9) | 0.0281 (4) |
| H15 | 0.1401 | 0.5650 | 0.1943 | 0.034* |
| C16 | 0.12928 (6) | 0.7355 (4) | 0.11388 (8) | 0.0238 (4) |
| O1 | 0.27352 (5) | 0.8741 (3) | 0.24925 (6) | 0.0359 (3) |
| H1O | 0.2644 | 0.7974 | 0.2157 | 0.043* |
| H2O | 0.2570 | 1.0234 | 0.2418 | 0.043* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0274 (8) | 0.0316 (9) | 0.0225 (8) | −0.0008 (7) | 0.0142 (7) | 0.0010 (7) |
| C1 | 0.0266 (10) | 0.0366 (11) | 0.0260 (10) | 0.0014 (8) | 0.0130 (8) | 0.0040 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0286 (10) | 0.0339 (11) | 0.0381 (11) | 0.0057 (8) | 0.0224 (9) | 0.0095 (9) |
| C3 | 0.0399 (11) | 0.0315 (10) | 0.0387 (11) | 0.0032 (9) | 0.0290 (10) | 0.0017 (9) |
| C4 | 0.0304 (10) | 0.0306 (10) | 0.0253 (9) | −0.0008 (8) | 0.0174 (8) | −0.0014 (8) |
| C5 | 0.0267 (9) | 0.0239 (9) | 0.0213 (8) | −0.0014 (7) | 0.0150 (7) | 0.0029 (7) |
| C6 | 0.0246 (9) | 0.0281 (10) | 0.0182 (8) | −0.0004 (7) | 0.0125 (7) | −0.0008 (7) |
| N2 | 0.0275 (8) | 0.0275 (8) | 0.0187 (7) | −0.0047 (6) | 0.0134 (6) | 0.0003 (6) |
| N3 | 0.0272 (8) | 0.0288 (8) | 0.0216 (8) | −0.0025 (6) | 0.0146 (7) | −0.0003 (6) |
| C7 | 0.0306 (10) | 0.0302 (10) | 0.0272 (9) | 0.0009 (8) | 0.0191 (8) | 0.0033 (8) |
| C8 | 0.0303 (10) | 0.0363 (11) | 0.0195 (9) | 0.0068 (8) | 0.0144 (8) | 0.0037 (8) |
| Cl1 | 0.0461 (3) | 0.0610 (4) | 0.0212 (2) | 0.0011 (3) | 0.0175 (2) | 0.0074 (2) |
| C9 | 0.0245 (9) | 0.0343 (11) | 0.0235 (9) | 0.0007 (8) | 0.0099 (8) | −0.0018 (8) |
| C10 | 0.0210 (9) | 0.0279 (10) | 0.0268 (9) | −0.0003 (7) | 0.0133 (8) | 0.0004 (8) |
| C11 | 0.0235 (9) | 0.0237 (9) | 0.0222 (9) | 0.0028 (7) | 0.0144 (7) | −0.0010 (7) |
| N4 | 0.0276 (8) | 0.0366 (9) | 0.0191 (7) | 0.0049 (7) | 0.0142 (7) | 0.0034 (7) |
| N5 | 0.0260 (8) | 0.0317 (9) | 0.0246 (8) | −0.0011 (7) | 0.0157 (7) | 0.0010 (7) |
| C12 | 0.0254 (9) | 0.0319 (10) | 0.0279 (10) | −0.0020 (8) | 0.0145 (8) | 0.0012 (8) |
| C13 | 0.0241 (9) | 0.0293 (10) | 0.0331 (10) | −0.0039 (8) | 0.0186 (8) | −0.0062 (8) |
| Cl2 | 0.0296 (3) | 0.0394 (3) | 0.0465 (3) | −0.0015 (2) | 0.0254 (2) | −0.0073 (2) |
| C14 | 0.0352 (10) | 0.0333 (10) | 0.0288 (10) | −0.0056 (8) | 0.0229 (9) | −0.0045 (8) |
| C15 | 0.0320 (10) | 0.0318 (10) | 0.0222 (9) | −0.0009 (8) | 0.0165 (8) | −0.0011 (8) |
| C16 | 0.0258 (9) | 0.0256 (9) | 0.0206 (8) | −0.0045 (7) | 0.0137 (7) | −0.0049 (7) |
| O1 | 0.0438 (8) | 0.0344 (8) | 0.0245 (7) | 0.0003 (6) | 0.0165 (6) | −0.0050 (6) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C1 | 1.337 (2) | C8—C9 | 1.381 (3) |
| N1—C5 | 1.343 (2) | C8—Cl1 | 1.7484 (18) |
| C1—C2 | 1.383 (3) | C9—C10 | 1.368 (3) |
| C1—H1 | 0.9500 | C9—H9 | 0.9500 |
| C2—C3 | 1.381 (3) | C10—C11 | 1.409 (2) |
| C2—H2 | 0.9500 | C10—H10 | 0.9500 |
| C3—C4 | 1.383 (3) | N4—C16 | 1.368 (2) |
| C3—H3 | 0.9500 | N4—H4N | 0.8698 |
| C4—C5 | 1.388 (3) | N5—C16 | 1.338 (2) |
| C4—H4 | 0.9500 | N5—C12 | 1.348 (2) |
| C5—C6 | 1.526 (2) | C12—C13 | 1.372 (3) |
| C6—N4 | 1.442 (2) | C12—H12 | 0.9500 |
| C6—N2 | 1.452 (2) | C13—C14 | 1.389 (3) |
| C6—H6 | 1.0000 | C13—Cl2 | 1.7418 (19) |
| N2—C11 | 1.358 (2) | C14—C15 | 1.365 (3) |
| N2—H2N | 0.8699 | C14—H14 | 0.9500 |
| N3—C7 | 1.342 (2) | C15—C16 | 1.413 (2) |
| N3—C11 | 1.344 (2) | C15—H15 | 0.9500 |
| C7—C8 | 1.375 (3) | O1—H1O | 0.8206 |
| C7—H7 | 0.9500 | O1—H2O | 0.8206 |
| | | | |
| C1—N1—C5 | 118.11 (16) | C9—C8—Cl1 | 121.13 (15) |
| N1—C1—C2 | 123.50 (18) | C10—C9—C8 | 118.51 (17) |

| | | | |
|---|---|---|---|
| N1—C1—H1 | 118.3 | C10—C9—H9 | 120.7 |
| C2—C1—H1 | 118.3 | C8—C9—H9 | 120.7 |
| C3—C2—C1 | 118.10 (18) | C9—C10—C11 | 119.16 (17) |
| C3—C2—H2 | 121.0 | C9—C10—H10 | 120.4 |
| C1—C2—H2 | 121.0 | C11—C10—H10 | 120.4 |
| C2—C3—C4 | 119.16 (18) | N3—C11—N2 | 117.63 (15) |
| C2—C3—H3 | 120.4 | N3—C11—C10 | 122.19 (16) |
| C4—C3—H3 | 120.4 | N2—C11—C10 | 120.16 (16) |
| C3—C4—C5 | 119.22 (18) | C16—N4—C6 | 123.43 (15) |
| C3—C4—H4 | 120.4 | C16—N4—H4N | 117.7 |
| C5—C4—H4 | 120.4 | C6—N4—H4N | 118.5 |
| N1—C5—C4 | 121.90 (16) | C16—N5—C12 | 117.83 (15) |
| N1—C5—C6 | 116.09 (15) | N5—C12—C13 | 123.00 (18) |
| C4—C5—C6 | 121.98 (16) | N5—C12—H12 | 118.5 |
| N4—C6—N2 | 110.65 (14) | C13—C12—H12 | 118.5 |
| N4—C6—C5 | 110.04 (14) | C12—C13—C14 | 119.23 (17) |
| N2—C6—C5 | 111.98 (15) | C12—C13—Cl2 | 120.28 (15) |
| N4—C6—H6 | 108.0 | C14—C13—Cl2 | 120.48 (14) |
| N2—C6—H6 | 108.0 | C15—C14—C13 | 118.88 (17) |
| C5—C6—H6 | 108.0 | C15—C14—H14 | 120.6 |
| C11—N2—C6 | 122.92 (15) | C13—C14—H14 | 120.6 |
| C11—N2—H2N | 117.7 | C14—C15—C16 | 118.96 (18) |
| C6—N2—H2N | 119.3 | C14—C15—H15 | 120.5 |
| C7—N3—C11 | 117.36 (15) | C16—C15—H15 | 120.5 |
| N3—C7—C8 | 123.29 (17) | N5—C16—N4 | 118.68 (16) |
| N3—C7—H7 | 118.4 | N5—C16—C15 | 122.09 (17) |
| C8—C7—H7 | 118.4 | N4—C16—C15 | 119.23 (16) |
| C7—C8—C9 | 119.47 (17) | H1O—O1—H2O | 106.9 |
| C7—C8—Cl1 | 119.40 (15) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*N*···N5$^{i}$ | 0.87 | 2.15 | 2.994 (2) | 165 |
| N4—H4*N*···O1$^{ii}$ | 0.87 | 2.18 | 2.993 (2) | 156 |
| O1—H1*O*···N1 | 0.82 | 1.98 | 2.773 (2) | 164 |
| O1—H2*O*···O1$^{iii}$ | 0.82 | 1.96 | 2.758 (2) | 163 |

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