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Crystal structure and Hirshfeld surface analysis and of 2-ammoniumylmethyl-1*H*-benzimidazol-3-ium chloride monohydrate. Corrigendum

Pinar Sen,[a] Sevgi Kansiz,[b] Necmi Dege,[b] S. Zeki Yildiz[c] and Galyna G. Tsapyuk[d]*

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In the paper by Sen *et al.* [*Acta Cryst.* (2018), E**74**, 1517–1520], the address of the correspondence author is incorrect.

In the paper by Sen *et al.* (2018), the address of the correspondence author, Galyna G. Tsapyuk, should be ‘Taras Shevchenko National University of Kyiv, Department of Chemistry, 64 Vladimirska Str., Kiev 01601, Ukraine’, as given above.

References

Sen, P., Kansiz, S., Dege, N., Yildiz, S. Z. & Tsapyuk, G. G. (2018). *Acta Cryst.* E**74**, 1517–1520.

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Crystal structure and Hirshfeld surface analysis and of 2-ammoniumylmethyl-1*H*-benzimidazol-3-ium chloride monohydrate

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Keywords: crystal structure; imidazol; ethanaminium; ethanaminium chloride; Hirshfeld surface.

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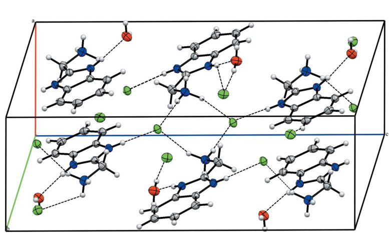
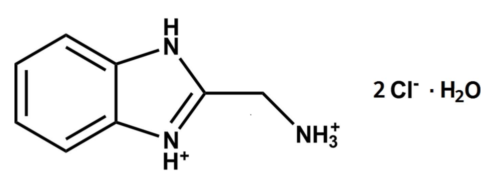


The asymmetric unit of the title compound, $C_8H_{11}N_3^{2+}\cdot 2Cl^-\cdot H_2O$, contains three organic cations, six chloride anions and three water molecules of crystallization, which are connected by extensive hydrogen-bonding interactions into a three-dimensional supramolecular architecture. Hirshfeld surface analysis and two-dimensional fingerprint plots indicate that the most important contributions to the crystal packing are from H···H (37.4%), Cl···H/H···Cl (35.5%), C···H/H···C (9.5%) and C···C (6.9%) interactions.

1. Chemical context

Heterocyclic compounds containing nitrogen such as benzimidazoles and their derivatives have attracted attention because of their medicinal applications as antiulcer, anticancer, antifungal, antimycobacterial and anti-inflammatory agents (El-masry *et al.*, 2000). Besides being important pharmacophores, in particular amine-substituted benzimidazoles are good intermediates for the synthesis of different organic compounds (Maurya *et al.*, 2007). General methods for the preparation of benzimidazoles involve the reaction of *o*-phenylenediamine and carboxylic acid or its derivatives under harsh dehydrating conditions or with aldehydes followed by oxidation (Peng *et al.*, 2014).



We report herein the compound 2-aminomethylbenzimidazole dihydrochloride (ambmz·2HCl) prepared as described previously (Wu *et al.*, 2008)

2. Structural commentary

The asymmetric unit of the title compound contains three organic cations, six chloride anions and three water molecules of crystallization, which are connected by O—H···Cl, N—H···O and N—H···Cl hydrogen bonds (Fig. 1). The r.m.s. deviations of the benzimidazolium ring systems are 0.0085 Å

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O1—H1$A$$\cdots$Cl4^{i}	0.82 (2)	2.63 (2)	3.4431 (15)	168 (3)
O1—H2$B$$\cdots$Cl2	0.81 (2)	2.36 (2)	3.1598 (18)	169 (3)
O2—H2$C$$\cdots$Cl3	0.82 (2)	2.33 (2)	3.1244 (17)	165 (2)
O2—H2$D$$\cdots$Cl1	0.81 (1)	2.64 (1)	3.4492 (15)	171 (3)
O3—H3$D$$\cdots$Cl5^{ii}	0.80 (2)	2.69 (2)	3.4586 (15)	164 (3)
O3—H3$E$$\cdots$Cl6^{ii}	0.82 (2)	2.32 (2)	3.1364 (18)	173 (3)
N1—H1$\cdots$O1	0.83 (2)	1.92 (2)	2.746 (2)	174 (2)
N2—H2$\cdots$Cl1^{iii}	0.71 (2)	2.44 (2)	3.1519 (17)	175 (2)
N3—H3$\cdots$Cl3	0.88 (3)	2.30 (3)	3.105 (2)	153 (2)
N3—H3$A$$\cdots$Cl1	0.86 (4)	2.26 (3)	3.119 (2)	173 (3)
N3—H3$B$$\cdots$Cl4^{iv}	0.99 (3)	2.33 (2)	3.267 (2)	156.8 (19)
N4—H4$A$$\cdots$O2	0.85 (2)	1.91 (2)	2.754 (2)	171 (2)
N5—H5$A$$\cdots$Cl5	0.83 (2)	2.31 (2)	3.1205 (17)	165 (2)
N6—H6$A$$\cdots$Cl2	0.87 (3)	2.33 (3)	3.107 (2)	150 (2)
N6—H6$B$$\cdots$Cl1^{v}	0.98 (3)	2.36 (2)	3.287 (2)	158.2 (18)
N6—H6$C$$\cdots$Cl4^{i}	0.79 (3)	2.35 (4)	3.1347 (19)	176 (3)
N7—H7$\cdots$O3	0.85 (3)	1.89 (3)	2.742 (2)	175 (3)
N8—H8$\cdots$Cl4	0.81 (2)	2.31 (2)	3.1049 (17)	172 (2)
N9—H9$A$$\cdots$Cl6	0.83 (3)	2.35 (3)	3.100 (2)	151 (2)
N9—H9$B$$\cdots$Cl5	0.80 (3)	2.32 (2)	3.120 (2)	176 (2)
N9—H9$C$$\cdots$Cl5^{vi}	0.99 (3)	2.34 (3)	3.270 (2)	157 (2)
C4—H4$\cdots$Cl1^{i}	0.92 (2)	2.81 (2)	3.535 (2)	136.7 (16)
C8—H8$B$$\cdots$Cl3^{vii}	0.93 (3)	2.65 (3)	3.544 (2)	162 (2)

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

for N1/N2/C1–C7, 0.0076 Å for N4/N5/C9–C15, 0.0063 Å for N7/N8/C17–C23 with maximum deviations from planarity of 0.0169 (13) Å for atom C7, 0.0149 (13) Å for atom C15 and 0.0132 (13) Å for atom C23, respectively. The observed bond lengths are in good agreement with previously reported values (Cui, 2011).

3. Supramolecular features

The crystal packing of the title compound features extensive hydrogen bonding (Table 1 and Fig. and 2) involving all three O atoms and all nine N atoms. N5—H5$A$$\cdots$Cl5, N8—H8$\cdots$Cl4, N2—H2$\cdots$Cl1^{ii}, N9—H9$C$$\cdots$Cl5^{vi} and N6—H6$B$$\cdots$Cl1^{v} hydrogen bonds link the ions into chains along the c-axis direction. These chains are linked by O–H$\cdots$Cl and N—H$\cdots$O hydrogen bonds, generating a three-dimensional network (Fig. 2).

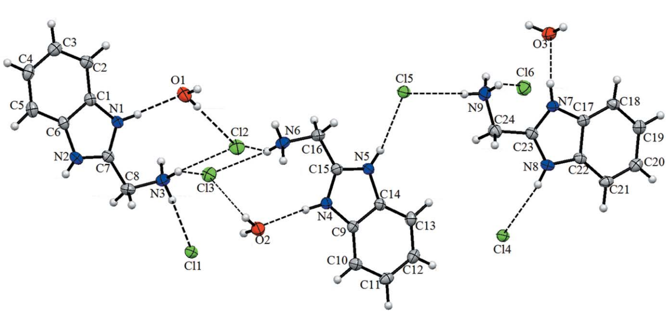


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 20% probability level.

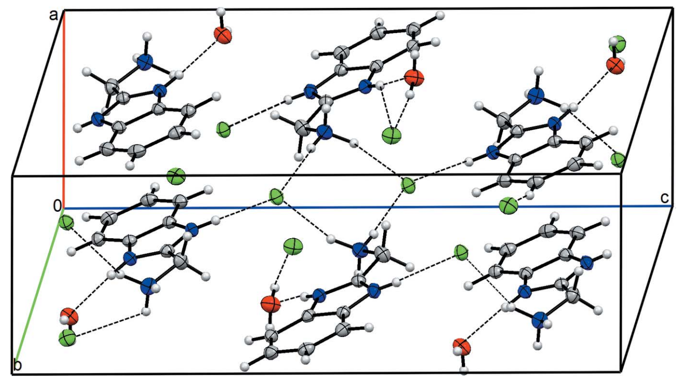


Figure 2
The view of the crystal packing of the title compound. Dashed lines denote the hydrogen bonds.

4. Hirshfeld surface analysis

The Hirshfeld surface analysis was performed using *Crystal Explorer* (Turner *et al.*, 2017). The Hirshfeld surfaces, illustrated in Fig. 3, and their associated two-dimensional fingerprint plots were used to quantify the various intermolecular

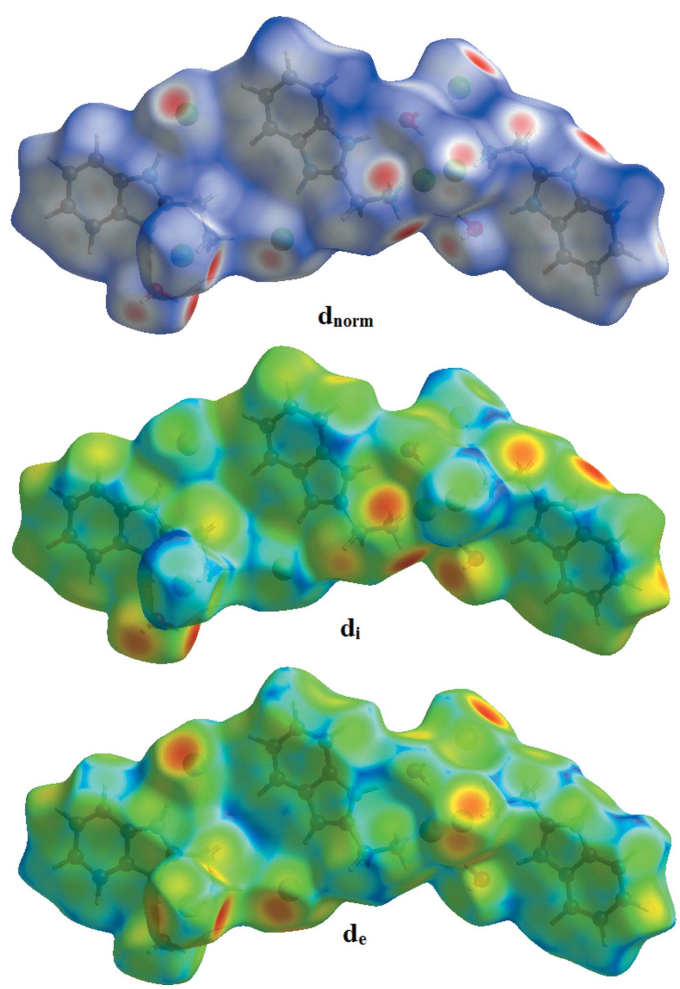


Figure 3
The Hirshfeld surface of the title compound mapped over d_{norm}, d_i and d_e.

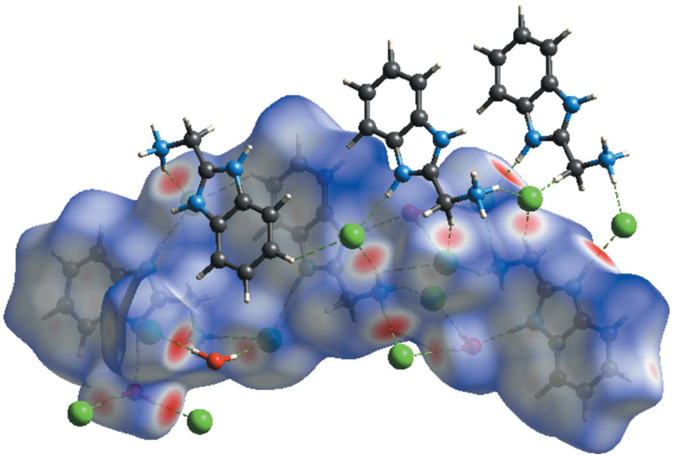


Figure 4
Hirshfeld surface mapped over d_{norm} to visualize the intermolecular interactions of the title compound.

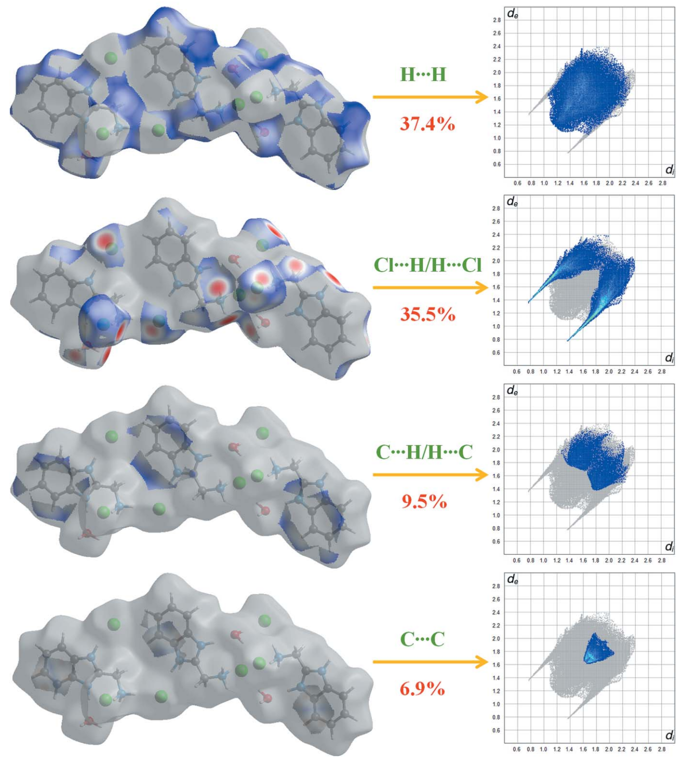


Figure 6
Two-dimensional fingerprint plots with a d_{norm} view of the H···H (37.4%), Cl···H/H···Cl (35.5%), C···H/H···C (9.5%) and C···C (6.9%) contacts in the title compound.

interactions in the synthesized complex. Red spots on the Hirshfeld surfaces indicate the intermolecular contacts involved in strong hydrogen bonds and interatomic contacts (Gümüş *et al.*, 2018; Kansız *et al.*, 2018; Kansız & Dege, 2018). The red spots in Fig. 4 correspond to the H···Cl contacts resulting from the N—H···Cl and O—H···Cl hydrogen bonds. The Hirshfeld surfaces were mapped using a standard (high) surface resolution with the three-dimensional d_{norm} surfaces mapped over a fixed colour scale of −0.518 (red) to 1.174 (blue) a.u..

Fig. 5 shows the two-dimensional fingerprint plot of all the contacts contributing to the Hirshfeld surface represented in normal mode. Fig. 6 shows the two-dimensional fingerprint plots of the (d_i, d_e) points associated with various atoms. H···H contacts contribute 37.4% to the Hirshfeld surface. The graph for Cl···H/H···Cl shows the contacts between the chlorine atoms inside the Hirshfeld surface and the hydrogen atoms outside the surface and *vice versa*, and has two symmetrical wings on the left and right sides (35.5%). Further, there are C···H/H···C (9.5%), C···C (6.9%), O···H/H···O (4.1%) and N···H/H···N (3.4%) contacts.

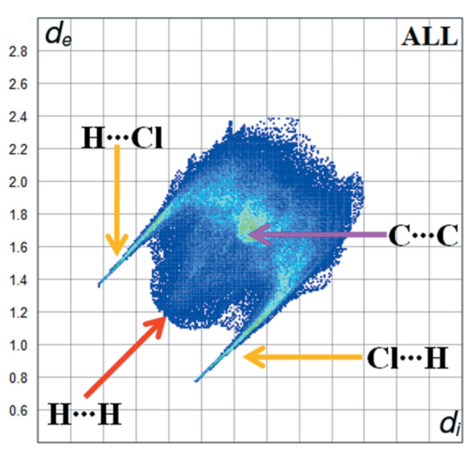


Figure 5
Fingerprint plot of all the contacts.

5. Synthesis and crystallization

o-Phenylenediamine (10.8 g, 99.87 mmol) and glycine (10.00 g, 133.2 mmol) were dissolved in 5.5 *M* HCl (150 mL) . The reaction mixture was purged by argon at room temperature and heated up to reflux temperature for 12 h. The reaction was monitored by TLC. After completion of the reaction, the mixture was concentrated to 50 mL and kept at 269 K for 2 d. The crystals were filtered off and washed twice with acetone and dried to give the desired product (Fig. 7).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically with C—H distances of 0.93–0.97 Å. and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. N-bound H atoms were located in difference-Fourier maps and refined isotropically. The coordinates of the water H atoms were determined from a difference-Fourier map and refined isotropically subject to a restraint of O—H = 0.82 (4) Å.

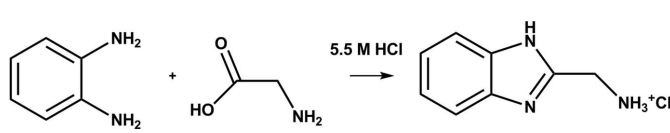


Figure 7
The synthesis of the title compound.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{11}N_3^+\cdot 2Cl^-\cdot H_2O\cdot$
M_r	238.11
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	6.9340 (4), 12.1198 (7), 19.2128 (11)
α, β, γ (°)	99.859 (5), 90.647 (5), 90.247 (5)
V (Å^3)	1590.64 (16)
Z	6
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.58
Crystal size (mm)	0.57 × 0.50 × 0.46
Data collection	
Diffractometer	Stoe IPDS 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.788, 0.828
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16045, 6254, 5000
R_{int}	0.064
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.092, 0.96
No. of reflections	6254
No. of parameters	536
No. of restraints	9
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.28

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXL2017/1* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

Acknowledgements

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supporting information

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Crystal structure and Hirshfeld surface analysis and of 2-ammonium-ylmethyl)-1*H*-benzimidazol-3-ium chloride monohydrate

Pinar Sen, Sevgi Kansiz, Necmi Dege, S. Zeki Yildiz and Galyna G. Tsapyuk

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *WinGX* (Farrugia, 2012); program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

2-Ammoniumylmethyl-1*H*-benzimidazol-3-ium chloride monohydrate

Crystal data

$C_8H_{11}N_3^+\cdot 2Cl^-\cdot H_2O\cdot$
M_r = 238.11
Triclinic, $P\overline{1}$
a = 6.9340 (4) Å
b = 12.1198 (7) Å
c = 19.2128 (11) Å
α = 99.859 (5)°
β = 90.647 (5)°
γ = 90.247 (5)°
V = 1590.64 (16) Å^3
Z = 6
F(000) = 744
D_x = 1.491 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 18110 reflections
θ = 1.7–27.4°
μ = 0.58 mm^{-1}
T = 296 K
Prism, brown
0.57 × 0.50 × 0.46 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)
T_{min} = 0.788, T_{max} = 0.828
16045 measured reflections
6254 independent reflections
5000 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 26.0°, θ_{min} = 1.7°
h = −8→8
k = −14→14
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 0.96
6254 reflections
536 parameters
9 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Extinction correction: SHELXL-2017/1 (Sheldrick 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0327 (17)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	1.44783 (7)	0.25544 (4)	0.93231 (2)	0.04012 (12)
Cl4	0.55220 (7)	0.93572 (4)	0.73215 (2)	0.03912 (12)
Cl5	0.44034 (7)	0.39635 (4)	0.59956 (2)	0.04089 (13)
Cl3	0.85067 (7)	0.04098 (4)	0.91238 (3)	0.04840 (14)
Cl6	−0.13546 (8)	0.60301 (5)	0.58937 (3)	0.05432 (15)
Cl2	1.13465 (8)	0.15568 (5)	0.74387 (3)	0.05337 (15)
O2	0.9557 (2)	0.29533 (13)	0.93050 (9)	0.0492 (3)
O1	1.0439 (2)	−0.10288 (14)	0.73035 (9)	0.0517 (4)
N4	0.7622 (2)	0.41261 (12)	0.84094 (8)	0.0332 (3)
O3	0.0525 (2)	0.64579 (14)	0.39493 (9)	0.0553 (4)
N7	0.2335 (2)	0.81071 (13)	0.48888 (8)	0.0333 (3)
N5	0.6592 (2)	0.46067 (13)	0.74372 (9)	0.0347 (3)
N1	1.2273 (2)	−0.21584 (13)	0.82407 (8)	0.0334 (3)
N2	1.3362 (2)	−0.25722 (14)	0.92226 (9)	0.0376 (4)
N8	0.3400 (2)	0.90994 (13)	0.58704 (9)	0.0358 (3)
N6	0.7067 (3)	0.17781 (15)	0.79023 (10)	0.0427 (4)
N9	0.2868 (3)	0.60170 (15)	0.53791 (10)	0.0447 (4)
N3	1.2803 (3)	0.02017 (15)	0.86850 (10)	0.0421 (4)
C14	0.7037 (2)	0.55975 (14)	0.78881 (9)	0.0314 (4)
C22	0.2942 (2)	0.98527 (15)	0.54300 (9)	0.0323 (4)
C9	0.7708 (2)	0.52904 (14)	0.85148 (9)	0.0315 (4)
C15	0.6935 (2)	0.37525 (15)	0.77671 (9)	0.0335 (4)
C1	1.2214 (2)	−0.33227 (14)	0.81587 (9)	0.0324 (4)
C17	0.2255 (2)	0.92225 (14)	0.48021 (9)	0.0319 (4)
C10	0.8268 (3)	0.60738 (16)	0.90934 (10)	0.0369 (4)
C18	0.1652 (2)	0.97150 (16)	0.42385 (10)	0.0355 (4)
C7	1.2981 (2)	−0.17423 (15)	0.88773 (9)	0.0339 (4)
C2	1.1642 (3)	−0.41361 (16)	0.75996 (10)	0.0377 (4)
C6	1.2930 (2)	−0.35839 (15)	0.87927 (10)	0.0349 (4)
C13	0.6926 (3)	0.67112 (16)	0.78093 (11)	0.0385 (4)
C23	0.3047 (2)	0.80652 (15)	0.55283 (9)	0.0342 (4)
C20	0.2469 (3)	1.15029 (16)	0.49646 (11)	0.0392 (4)
C21	0.3055 (3)	1.10154 (16)	0.55279 (11)	0.0382 (4)
C12	0.7490 (3)	0.74911 (16)	0.83844 (11)	0.0394 (4)
C5	1.3092 (3)	−0.46915 (17)	0.88878 (11)	0.0421 (4)

C19	0.1785 (3)	1.08684 (16)	0.43313 (10)	0.0389 (4)
C4	1.2532 (3)	−0.54982 (17)	0.83351 (12)	0.0443 (5)
C11	0.8145 (3)	0.71817 (16)	0.90146 (11)	0.0401 (4)
C8	1.3424 (3)	−0.05475 (17)	0.91637 (11)	0.0414 (4)
C16	0.6469 (3)	0.25681 (17)	0.74466 (11)	0.0428 (4)
C3	1.1819 (3)	−0.52313 (17)	0.77020 (12)	0.0423 (4)
C24	0.3525 (3)	0.70519 (18)	0.58323 (12)	0.0458 (5)
H2	1.384 (3)	−0.2526 (17)	0.9558 (11)	0.028 (5)*
H18	0.111 (3)	0.9325 (18)	0.3840 (12)	0.044 (6)*
H10	0.873 (3)	0.5879 (16)	0.9522 (11)	0.033 (5)*
H2A	1.108 (3)	−0.3947 (17)	0.7161 (11)	0.039 (5)*
H11	0.854 (3)	0.7742 (19)	0.9433 (11)	0.046 (6)*
H19	0.136 (3)	1.1218 (17)	0.3927 (11)	0.039 (5)*
H20	0.255 (3)	1.223 (2)	0.5012 (12)	0.048 (6)*
H13	0.649 (3)	0.6891 (17)	0.7361 (11)	0.039 (5)*
H12	0.740 (3)	0.816 (2)	0.8342 (12)	0.050 (6)*
H21	0.350 (3)	1.1439 (19)	0.5987 (12)	0.047 (6)*
H5	1.355 (3)	−0.4842 (19)	0.9333 (12)	0.050 (6)*
H4	1.264 (3)	−0.6238 (19)	0.8385 (11)	0.040 (5)*
H5A	0.608 (3)	0.4556 (18)	0.7041 (12)	0.041 (6)*
H1	1.179 (3)	−0.179 (2)	0.7956 (13)	0.055 (7)*
H4A	0.811 (3)	0.372 (2)	0.8683 (12)	0.052 (6)*
H8	0.393 (3)	0.9236 (17)	0.6251 (12)	0.036 (5)*
H24A	0.291 (3)	0.710 (2)	0.6289 (13)	0.058 (7)*
H24B	0.491 (5)	0.697 (3)	0.5884 (17)	0.101 (10)*
H7	0.183 (4)	0.757 (2)	0.4601 (14)	0.063 (7)*
H9A	0.167 (4)	0.600 (2)	0.5354 (13)	0.058 (7)*
H16A	0.518 (4)	0.253 (2)	0.7334 (15)	0.076 (8)*
H9B	0.325 (4)	0.551 (2)	0.5559 (13)	0.055 (7)*
H9C	0.336 (4)	0.593 (2)	0.4891 (16)	0.080 (9)*
H16B	0.709 (3)	0.2385 (19)	0.7019 (13)	0.052 (6)*
H3C	1.143 (3)	−0.581 (2)	0.7340 (12)	0.050 (6)*
H8A	1.472 (4)	−0.045 (2)	0.9269 (13)	0.061 (7)*
H8B	1.282 (4)	−0.035 (2)	0.9596 (14)	0.066 (7)*
H6A	0.831 (4)	0.176 (2)	0.7947 (13)	0.061 (8)*
H6B	0.660 (3)	0.194 (2)	0.8388 (14)	0.059 (7)*
H6C	0.667 (4)	0.118 (3)	0.7738 (15)	0.065 (8)*
H2C	0.920 (3)	0.2322 (16)	0.9337 (14)	0.063 (8)*
H2D	1.072 (2)	0.289 (2)	0.9267 (17)	0.098 (12)*
H3A	1.316 (4)	0.087 (3)	0.8871 (16)	0.086 (10)*
H3B	1.330 (3)	0.000 (2)	0.8197 (14)	0.060 (7)*
H3	1.154 (4)	0.022 (2)	0.8652 (12)	0.056 (7)*
H3D	−0.062 (3)	0.649 (3)	0.3941 (19)	0.106 (12)*
H3E	0.082 (4)	0.5804 (16)	0.3962 (15)	0.071 (9)*
H1A	0.926 (3)	−0.102 (3)	0.7339 (18)	0.100 (12)*
H2B	1.076 (4)	−0.0391 (16)	0.7286 (15)	0.069 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0439 (2)	0.0399 (2)	0.0360 (2)	0.00037 (18)	−0.00373 (18)	0.00530 (18)
Cl4	0.0430 (2)	0.0388 (2)	0.0348 (2)	−0.00156 (18)	−0.00346 (18)	0.00436 (18)
Cl5	0.0447 (3)	0.0395 (2)	0.0378 (2)	−0.00330 (18)	−0.00542 (18)	0.00547 (18)
Cl3	0.0486 (3)	0.0458 (3)	0.0518 (3)	−0.0026 (2)	0.0038 (2)	0.0112 (2)
Cl6	0.0503 (3)	0.0508 (3)	0.0615 (3)	0.0005 (2)	−0.0013 (2)	0.0085 (2)
Cl2	0.0491 (3)	0.0519 (3)	0.0600 (3)	−0.0049 (2)	−0.0007 (2)	0.0126 (2)
O2	0.0490 (9)	0.0458 (9)	0.0538 (9)	−0.0016 (7)	−0.0076 (7)	0.0121 (7)
O1	0.0475 (9)	0.0546 (9)	0.0566 (9)	−0.0045 (7)	−0.0098 (7)	0.0209 (8)
N4	0.0346 (7)	0.0320 (7)	0.0337 (8)	0.0003 (6)	−0.0023 (6)	0.0071 (6)
O3	0.0496 (9)	0.0456 (9)	0.0652 (10)	0.0011 (7)	−0.0110 (8)	−0.0056 (7)
N7	0.0323 (7)	0.0331 (8)	0.0331 (8)	−0.0025 (6)	−0.0008 (6)	0.0017 (6)
N5	0.0336 (8)	0.0387 (8)	0.0314 (8)	0.0013 (6)	−0.0032 (6)	0.0047 (6)
N1	0.0317 (7)	0.0359 (8)	0.0341 (8)	−0.0008 (6)	−0.0022 (6)	0.0106 (6)
N2	0.0333 (8)	0.0494 (10)	0.0314 (9)	−0.0017 (7)	−0.0053 (7)	0.0107 (7)
N8	0.0342 (8)	0.0420 (9)	0.0298 (8)	−0.0059 (6)	−0.0038 (6)	0.0028 (6)
N6	0.0505 (11)	0.0310 (9)	0.0451 (10)	−0.0057 (8)	0.0012 (8)	0.0025 (7)
N9	0.0501 (11)	0.0375 (9)	0.0485 (11)	0.0051 (8)	0.0010 (8)	0.0128 (8)
N3	0.0469 (10)	0.0358 (9)	0.0426 (10)	−0.0042 (7)	0.0018 (8)	0.0034 (7)
C14	0.0264 (8)	0.0346 (9)	0.0331 (9)	0.0007 (6)	0.0018 (7)	0.0052 (7)
C22	0.0265 (8)	0.0378 (9)	0.0315 (9)	−0.0035 (7)	0.0011 (7)	0.0027 (7)
C9	0.0275 (8)	0.0312 (8)	0.0357 (9)	−0.0003 (6)	0.0023 (7)	0.0054 (7)
C15	0.0295 (8)	0.0347 (9)	0.0353 (9)	0.0001 (7)	0.0003 (7)	0.0029 (7)
C1	0.0266 (8)	0.0355 (9)	0.0361 (9)	−0.0010 (7)	0.0026 (7)	0.0093 (7)
C17	0.0274 (8)	0.0337 (9)	0.0334 (9)	−0.0023 (6)	0.0034 (7)	0.0019 (7)
C10	0.0349 (9)	0.0406 (10)	0.0343 (9)	−0.0015 (7)	0.0003 (7)	0.0042 (8)
C18	0.0306 (8)	0.0423 (10)	0.0320 (9)	−0.0003 (7)	0.0002 (7)	0.0016 (8)
C7	0.0287 (8)	0.0391 (9)	0.0343 (9)	−0.0018 (7)	0.0006 (7)	0.0073 (7)
C2	0.0319 (9)	0.0440 (10)	0.0371 (10)	−0.0025 (7)	0.0017 (7)	0.0066 (8)
C6	0.0269 (8)	0.0417 (10)	0.0378 (9)	0.0014 (7)	0.0008 (7)	0.0112 (8)
C13	0.0334 (9)	0.0399 (10)	0.0442 (11)	0.0032 (7)	0.0036 (8)	0.0130 (8)
C23	0.0291 (8)	0.0384 (9)	0.0353 (9)	−0.0026 (7)	0.0008 (7)	0.0066 (7)
C20	0.0344 (9)	0.0343 (10)	0.0485 (11)	−0.0028 (8)	0.0075 (8)	0.0051 (8)
C21	0.0318 (9)	0.0384 (10)	0.0408 (10)	−0.0061 (7)	0.0020 (8)	−0.0030 (8)
C12	0.0359 (9)	0.0307 (9)	0.0519 (12)	0.0024 (7)	0.0068 (8)	0.0076 (8)
C5	0.0339 (9)	0.0470 (11)	0.0498 (12)	0.0041 (8)	0.0033 (8)	0.0202 (9)
C19	0.0349 (9)	0.0419 (10)	0.0412 (10)	0.0012 (7)	0.0053 (8)	0.0100 (8)
C4	0.0354 (10)	0.0389 (10)	0.0608 (13)	0.0044 (8)	0.0106 (9)	0.0146 (10)
C11	0.0351 (9)	0.0367 (10)	0.0457 (11)	−0.0036 (7)	0.0058 (8)	−0.0013 (8)
C8	0.0423 (11)	0.0437 (11)	0.0362 (10)	−0.0059 (8)	−0.0033 (9)	0.0017 (8)
C16	0.0494 (12)	0.0369 (10)	0.0398 (11)	−0.0013 (8)	−0.0073 (9)	−0.0001 (8)
C3	0.0349 (9)	0.0401 (10)	0.0509 (12)	−0.0025 (8)	0.0069 (8)	0.0044 (9)
C24	0.0478 (11)	0.0460 (11)	0.0456 (12)	−0.0031 (9)	−0.0062 (9)	0.0141 (9)

Geometric parameters (Å, º)

O2—H2C	0.817 (16)	C22—C17	1.391 (2)
O2—H2D	0.812 (17)	C22—C21	1.391 (3)
O1—H1A	0.819 (17)	C9—C10	1.383 (3)
O1—H2B	0.810 (16)	C15—C16	1.494 (3)
N1—C7	1.328 (2)	C1—C2	1.381 (3)
N1—C1	1.393 (2)	C1—C6	1.396 (2)
N1—H1	0.83 (2)	C17—C18	1.384 (2)
N2—C7	1.322 (2)	C10—C11	1.380 (3)
N2—C6	1.386 (3)	C10—H10	0.95 (2)
N2—H2	0.71 (2)	C18—C19	1.381 (3)
N3—C8	1.461 (3)	C18—H18	0.91 (2)
N3—H3A	0.87 (4)	C7—C8	1.488 (3)
N3—H3B	0.99 (3)	C2—C3	1.381 (3)
N3—H3	0.88 (3)	C2—H2A	0.99 (2)
N4—C15	1.322 (2)	C6—C5	1.390 (3)
N4—C9	1.392 (2)	C13—C12	1.377 (3)
N4—H4A	0.85 (2)	C13—H13	0.97 (2)
N5—C15	1.324 (2)	C23—C24	1.484 (3)
N5—C14	1.386 (2)	C20—C21	1.377 (3)
N5—H5A	0.83 (2)	C20—C19	1.400 (3)
N6—C16	1.462 (3)	C20—H20	0.87 (2)
N6—H6A	0.86 (3)	C21—H21	0.99 (2)
N6—H6B	0.98 (3)	C12—C11	1.399 (3)
N6—H6C	0.79 (3)	C12—H12	0.83 (2)
O3—H3D	0.796 (17)	C5—C4	1.366 (3)
O3—H3E	0.822 (16)	C5—H5	0.96 (2)
N7—C23	1.328 (2)	C19—H19	0.99 (2)
N7—C17	1.391 (2)	C4—C3	1.397 (3)
N7—H7	0.85 (3)	C4—H4	0.92 (2)
N8—C23	1.332 (2)	C11—H11	0.99 (2)
N8—C22	1.383 (2)	C8—H8A	0.92 (3)
N8—H8	0.80 (2)	C8—H8B	0.93 (3)
N9—C24	1.467 (3)	C16—H16A	0.92 (3)
N9—H9A	0.83 (3)	C16—H16B	0.93 (2)
N9—H9B	0.80 (3)	C3—H3C	0.93 (2)
N9—H9C	0.99 (3)	C24—H24A	0.97 (2)
C14—C13	1.386 (2)	C24—H24B	0.97 (3)
C14—C9	1.395 (2)		
H2C—O2—H2D	104 (2)	C19—C18—C17	116.33 (18)
H1A—O1—H2B	106 (2)	C19—C18—H18	120.3 (14)
C15—N4—C9	108.99 (15)	C17—C18—H18	123.2 (14)
C15—N4—H4A	124.8 (16)	N2—C7—N1	109.33 (16)
C9—N4—H4A	125.4 (16)	N2—C7—C8	123.45 (17)
H3D—O3—H3E	107 (2)	N1—C7—C8	127.11 (16)
C23—N7—C17	108.55 (16)	C3—C2—C1	116.08 (18)

C23—N7—H7	126.6 (17)	C3—C2—H2A	121.8 (12)
C17—N7—H7	124.0 (17)	C1—C2—H2A	122.0 (12)
C15—N5—C14	109.14 (15)	N2—C6—C5	132.85 (18)
C15—N5—H5A	124.9 (15)	N2—C6—C1	106.35 (15)
C14—N5—H5A	125.6 (15)	C5—C6—C1	120.80 (18)
C7—N1—C1	109.27 (15)	C12—C13—C14	116.35 (17)
C7—N1—H1	125.7 (17)	C12—C13—H13	124.6 (12)
C1—N1—H1	124.5 (17)	C14—C13—H13	119.1 (12)
C7—N2—C6	109.38 (16)	N7—C23—N8	109.72 (16)
C7—N2—H2	126.4 (17)	N7—C23—C24	127.55 (18)
C6—N2—H2	123.7 (17)	N8—C23—C24	122.63 (17)
C23—N8—C22	108.85 (15)	C21—C20—C19	122.08 (18)
C23—N8—H8	123.7 (15)	C21—C20—H20	117.6 (16)
C22—N8—H8	127.0 (15)	C19—C20—H20	120.3 (15)
C16—N6—H6A	111.4 (17)	C20—C21—C22	116.12 (18)
C16—N6—H6B	115.5 (14)	C20—C21—H21	124.1 (13)
H6A—N6—H6B	104 (2)	C22—C21—H21	119.7 (13)
C16—N6—H6C	109 (2)	C13—C12—C11	122.09 (18)
H6A—N6—H6C	110 (3)	C13—C12—H12	116.6 (16)
H6B—N6—H6C	107 (2)	C11—C12—H12	121.3 (16)
C24—N9—H9A	110.4 (18)	C4—C5—C6	116.97 (18)
C24—N9—H9B	106.7 (18)	C4—C5—H5	124.2 (14)
H9A—N9—H9B	109 (2)	C6—C5—H5	118.8 (14)
C24—N9—H9C	113.6 (17)	C18—C19—C20	121.68 (18)
H9A—N9—H9C	108 (2)	C18—C19—H19	116.2 (12)
H9B—N9—H9C	109 (2)	C20—C19—H19	122.1 (12)
C8—N3—H3A	108 (2)	C5—C4—C3	121.94 (19)
C8—N3—H3B	114.2 (14)	C5—C4—H4	118.4 (13)
H3A—N3—H3B	111 (2)	C3—C4—H4	119.6 (13)
C8—N3—H3	111.0 (16)	C10—C11—C12	121.71 (19)
H3A—N3—H3	106 (3)	C10—C11—H11	115.9 (12)
H3B—N3—H3	107 (2)	C12—C11—H11	122.3 (12)
C13—C14—N5	132.44 (17)	N3—C8—C7	112.34 (16)
C13—C14—C9	121.46 (17)	N3—C8—H8A	110.4 (16)
N5—C14—C9	106.11 (15)	C7—C8—H8A	110.8 (16)
N8—C22—C17	106.45 (15)	N3—C8—H8B	109.5 (16)
N8—C22—C21	131.74 (17)	C7—C8—H8B	109.3 (16)
C17—C22—C21	121.81 (17)	H8A—C8—H8B	104 (2)
C10—C9—N4	131.77 (16)	N6—C16—C15	112.13 (17)
C10—C9—C14	122.19 (16)	N6—C16—H16A	113.4 (18)
N4—C9—C14	106.02 (15)	C15—C16—H16A	108.1 (18)
N4—C15—N5	109.73 (16)	N6—C16—H16B	108.5 (14)
N4—C15—C16	127.44 (16)	C15—C16—H16B	109.5 (15)
N5—C15—C16	122.72 (16)	H16A—C16—H16B	105 (2)
C2—C1—N1	131.96 (16)	C2—C3—C4	121.8 (2)
C2—C1—C6	122.37 (17)	C2—C3—H3C	118.8 (14)
N1—C1—C6	105.66 (16)	C4—C3—H3C	119.4 (14)
C18—C17—C22	121.97 (16)	N9—C24—C23	112.39 (17)

C18—C17—N7	131.61 (17)	N9—C24—H24A	108.5 (15)
C22—C17—N7	106.41 (15)	C23—C24—H24A	109.0 (14)
C11—C10—C9	116.19 (17)	N9—C24—H24B	105 (2)
C11—C10—H10	120.6 (12)	C23—C24—H24B	112 (2)
C9—C10—H10	123.2 (12)	H24A—C24—H24B	110 (2)

C15—N5—C14—C13	−179.30 (18)	C7—N2—C6—C5	178.55 (18)
C15—N5—C14—C9	0.93 (19)	C7—N2—C6—C1	−1.15 (19)
C23—N8—C22—C17	1.03 (19)	C2—C1—C6—N2	179.60 (15)
C23—N8—C22—C21	−179.49 (17)	N1—C1—C6—N2	0.52 (18)
C15—N4—C9—C10	178.27 (18)	C2—C1—C6—C5	−0.1 (3)
C15—N4—C9—C14	−0.41 (18)	N1—C1—C6—C5	−179.23 (15)
C13—C14—C9—C10	1.1 (3)	N5—C14—C13—C12	179.48 (17)
N5—C14—C9—C10	−179.15 (15)	C9—C14—C13—C12	−0.8 (2)
C13—C14—C9—N4	179.89 (15)	C17—N7—C23—N8	1.29 (19)
N5—C14—C9—N4	−0.31 (18)	C17—N7—C23—C24	−175.17 (18)
C9—N4—C15—N5	1.02 (19)	C22—N8—C23—N7	−1.5 (2)
C9—N4—C15—C16	−175.38 (18)	C22—N8—C23—C24	175.21 (16)
C14—N5—C15—N4	−1.22 (19)	C19—C20—C21—C22	0.5 (3)
C14—N5—C15—C16	175.38 (16)	N8—C22—C21—C20	179.87 (17)
C7—N1—C1—C2	−178.68 (18)	C17—C22—C21—C20	−0.7 (2)
C7—N1—C1—C6	0.28 (18)	C14—C13—C12—C11	0.2 (3)
N8—C22—C17—C18	179.76 (15)	N2—C6—C5—C4	−179.37 (18)
C21—C22—C17—C18	0.2 (2)	C1—C6—C5—C4	0.3 (3)
N8—C22—C17—N7	−0.25 (17)	C17—C18—C19—C20	−0.8 (3)
C21—C22—C17—N7	−179.79 (15)	C21—C20—C19—C18	0.3 (3)
C23—N7—C17—C18	179.37 (18)	C6—C5—C4—C3	−0.3 (3)
C23—N7—C17—C22	−0.62 (18)	C9—C10—C11—C12	0.0 (3)
N4—C9—C10—C11	−179.14 (17)	C13—C12—C11—C10	0.2 (3)
C14—C9—C10—C11	−0.6 (2)	N2—C7—C8—N3	−178.27 (17)
C22—C17—C18—C19	0.5 (2)	N1—C7—C8—N3	6.0 (3)
N7—C17—C18—C19	−179.44 (17)	N4—C15—C16—N6	−6.7 (3)
C6—N2—C7—N1	1.4 (2)	N5—C15—C16—N6	177.37 (17)
C6—N2—C7—C8	−175.02 (16)	C1—C2—C3—C4	0.1 (3)
C1—N1—C7—N2	−1.02 (19)	C5—C4—C3—C2	0.1 (3)
C1—N1—C7—C8	175.20 (17)	N7—C23—C24—N9	−8.3 (3)
N1—C1—C2—C3	178.75 (17)	N8—C23—C24—N9	175.69 (17)
C6—C1—C2—C3	−0.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Cl4^{i}	0.82 (2)	2.63 (2)	3.4431 (15)	168 (3)
O1—H2*B*···Cl2	0.81 (2)	2.36 (2)	3.1598 (18)	169 (3)
O2—H2*C*···Cl3	0.82 (2)	2.33 (2)	3.1244 (17)	165 (2)
O2—H2*D*···Cl1	0.81 (1)	2.64 (1)	3.4492 (15)	171 (3)
O3—H3*D*···Cl5^{ii}	0.80 (2)	2.69 (2)	3.4586 (15)	164 (3)
O3—H3*E*···Cl6^{ii}	0.82 (2)	2.32 (2)	3.1364 (18)	173 (3)

N1—H1···O1	0.83 (2)	1.92 (2)	2.746 (2)	174 (2)
N2—H2···Cl1[iii]	0.71 (2)	2.44 (2)	3.1519 (17)	175 (2)
N3—H3···Cl3	0.88 (3)	2.30 (3)	3.105 (2)	153 (2)
N3—H3*A*···Cl1	0.86 (4)	2.26 (3)	3.119 (2)	173 (3)
N3—H3*B*···Cl4[iv]	0.99 (3)	2.33 (2)	3.267 (2)	156.8 (19)
N4—H4*A*···O2	0.85 (2)	1.91 (2)	2.754 (2)	171 (2)
N5—H5*A*···Cl5	0.83 (2)	2.31 (2)	3.1205 (17)	165 (2)
N6—H6*A*···Cl2	0.87 (3)	2.33 (3)	3.107 (2)	150 (2)
N6—H6*B*···Cl1[v]	0.98 (3)	2.36 (2)	3.287 (2)	158.2 (18)
N6—H6*C*···Cl4[i]	0.79 (3)	2.35 (4)	3.1347 (19)	176 (3)
N7—H7···O3	0.85 (3)	1.89 (3)	2.742 (2)	175 (3)
N8—H8···Cl4	0.81 (2)	2.31 (2)	3.1049 (17)	172 (2)
N9—H9*A*···Cl6	0.83 (3)	2.35 (3)	3.100 (2)	151 (2)
N9—H9*B*···Cl5	0.80 (3)	2.32 (2)	3.120 (2)	176 (2)
N9—H9*C*···Cl5[vi]	0.99 (3)	2.34 (3)	3.270 (2)	157 (2)
C4—H4···Cl1[i]	0.92 (2)	2.81 (2)	3.535 (2)	136.7 (16)
C8—H8*B*···Cl3[vii]	0.93 (3)	2.65 (3)	3.544 (2)	162 (2)

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