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2-(1,2,3,4-Tetrahydro-1-naphthyl)-imidazolium chloride monohydrate

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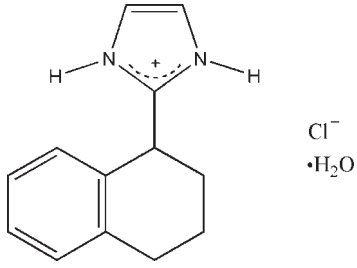
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.033; wR factor = 0.091; data-to-parameter ratio = 12.3.

In the title compound, $C_{13}H_{15}N_2^+\cdot Cl^-\cdot H_2O$, the ions and water molecules are connected by N—H···Cl, O—H···Cl, NH···Cl···HO, NH···Cl···HN and OH···Cl···HO interactions, forming discrete $D(2)$ and $D_2^1(3)$ chains, $C_2^1(6)$ chains and $R_4^2(8)$ rings, leading to a neutral two-dimensional network. The crystal structure is further stabilized by π–π stacking interactions [centroid–centroid distance = 3.652 (11) Å].

Related literature

The title compound is a by-product obtained in the preparation of the popular decongestant tetrahydrozoline hydrochloride and differs from the main product in the presence of an aromatic imidazole instead of a dihydroimidazole group. For the structure of the tetrahydrozoline main product, see: Ghose & Dattagupta (1989); Ciattini *et al.* (2010). For the identification of the nature of the title compound, see: Bartolucci (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{13}H_{15}N_2^+\cdot Cl^-\cdot H_2O$
M_r = 252.74
Monoclinic, $P2_1/n$
a = 9.8299 (1) Å
b = 12.6671 (2) Å
c = 10.5375 (2) Å
β = 92.666 (1)°
V = 1310.67 (3) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 2.46 mm^{-1}
T = 173 K
0.40 × 0.25 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur PX Ultra CCD diffractometer
Absorption correction: multi-scan (*ABSPACK*; Oxford Diffraction, 2006)
T_{min} = 0.594, T_{max} = 1.000
3831 measured reflections
1981 independent reflections
1883 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 61.6°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.091
S = 1.09
1981 reflections
161 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H14···Cl^{i}	0.88	2.21	3.0897 (16)	176
N2—H15···Cl^{ii}	0.88	2.25	3.1164 (15)	169
O—H17···Cl	0.86 (1)	2.41 (1)	3.2612 (18)	173 (3)
O—H16···Cl^{iii}	0.86 (1)	2.37 (1)	3.2252 (17)	175 (3)

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

Data collection: *CrysAlis PRO CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO CCD*; data reduction: *CrysAlis PRO RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SIR2004* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2288).

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2-(1,2,3,4-Tetrahydro-1-naphthyl)imidazolium chloride monohydrate

Bruno Bruni, Gianluca Bartolucci, Samuele Ciattini and Silvia Coran

S1. Comment

The industrial preparation of the widely used drug tetrahydrozolyne hydrochloride, 2-(1,2,3,4-tetrahydro-naphthalen-1-yl)-4,5- dihydro-1 *H*-imidazole hydrochloride, whose structure was reported several years ago (Ghose & Dattagupta, 1989), is generally accompanied by tiny amounts of an impurity (the title compound), whose nature has been identified (Bartolucci, 2010), but whose structure awaited investigation.

The trace byproduct, strictly related to the tetrahydrozolyne molecule, features an imidazole, rather than a dihydro-imidazole ring. The structure of the present hydrochloride consists of cations, generated by *N*-protonation of the above imidazole derivative, chloride anions and solvate water molecules in 1:1:1 ratios. The content of the asymmetric unit is shown in Fig. 1. In the course of our investigations on these species, the structure of the main product of the preparation, already known (Ghose & Dattagupta, 1989), has been refined against low–temperature data and deposited at the Cambridge Structural database (deposition number CCDC 782942 [Ciattini *et al.*, (2010)]. In spite of the above difference between molecules of the main product and of the impurity and irrespective of different packing modes in the two structures, the overall molecular geometries are closely similar: *e.g.*, the dihedral angle formed by the best planes through the benzene and imidazole rings is 88.62 (5)° in the cation of the present structure and 88.00 (6)° in that of the tetrahydrozoline hydrochloride drug (170 K data).The structure of (I), $C_{13}H_{15}N_2^+.Cl^-.H_2O$, comprises discrete ions and water molecules which are interconnected by N—H···Cl, O—H···Cl, NH···Cl···HO, NH···Cl···HN and OH···Cl···HO interactions to form discrete chains D(2), $D_2^1(3)$; chains , $C^1_2(6)$ and rings $R_4^2(8)$ motifs (Bernstein *et al.*, 1995), leading to a neutral bidimensional- network. The crystal structure is further stabilized by π-π stacking interactions, (Cg1-Cg2= 3.652 (11) Å, α = 6.59 (10)° (Cg1 = N1/C1-C2/N2/C3 and Cg2 = C8-C13) and this interaction is not observed in the crystal structure of the tetrahydrozoline main product (Ghose & Dattagupta, 1989; Ciattini *et al.*, 2010).

S2. Experimental

Samples of the compound, made available from concomitant studies (Bartolucci, 2010), were obtained in suitable form for X-ray diffraction analysis by slow evaporation from methanolic solutions.

S3. Refinement

In the final refinement cycles non-hydrogen atoms were assigned anisotropic thermal parameters and H atoms had U_{iso}(H) = 1.2 U_{eq}(C, *N*), or U_{iso}(H) = 1.5 U_{eq}(O) for the water H atoms. Hydrogen atoms were placed in geometrically generated positions, riding, except for those of the water molecule, whose positions were refined with a restraint on O—H distances (0.86 (1) Å final value). Assigned C—H: tertiary CH 1.00 Å, secondary CH_2 0.99 Å, aromatic CH 0.95 Å. Aromatic N—H: 0.88 Å.

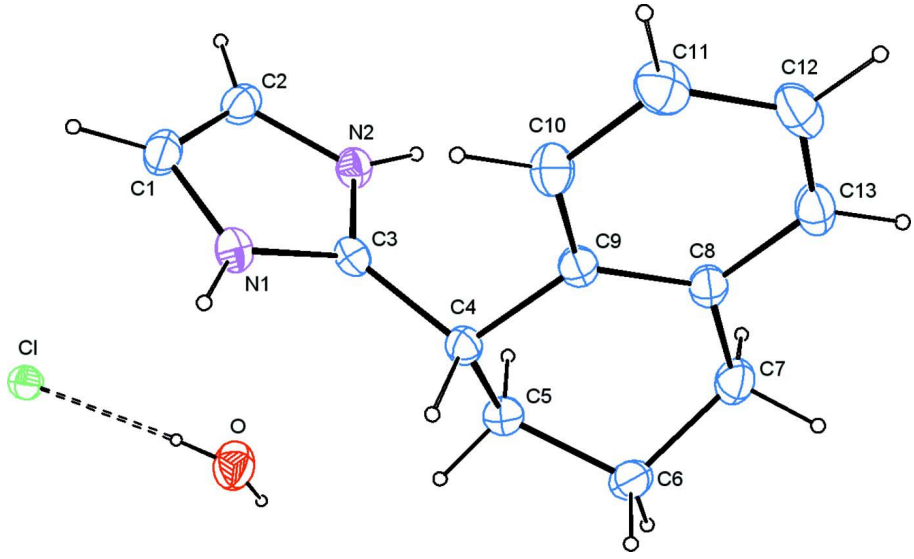

Figure 1

A view of the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. A hydrogen bond is denoted by a dashed line.The labelling criterion used for the structure of the related tetrahydrozoline hydrochloride has been preserved.

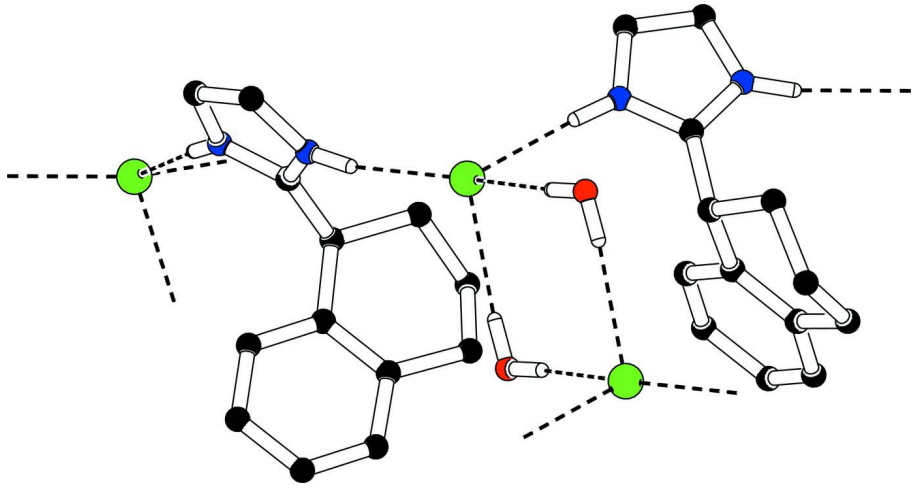

Figure 2

A view of the arrangement of hydrogen bonds in the structure of the title compound. Only hydrogen atoms involved in the formation of hydrogen bonds are shown for clarity. Hydrogen bonds are denoted by dashed lines.

2-(1,2,3,4-Tetrahydro-1-naphthyl)imidazolium chloride monohydrate

Crystal data

$C_{13}H_{15}N_2^+ \cdot Cl^- \cdot H_2O$
$M_r = 252.74$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 9.8299$ (1) Å
$b = 12.6671$ (2) Å
$c = 10.5375$ (2) Å
$\beta = 92.666$ (1)°
$V = 1310.67$ (3) Å^3
$Z = 4$
$F(000) = 536$
$D_x = 1.281$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54180$ Å
Cell parameters from 3348 reflections

θ = 4.2–61.4°
μ = 2.46 mm^{-1}
T = 173 K

Irregularly shaped prism, colourless
0.40 × 0.25 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur PX Ultra CCD diffractometer
Radiation source: fine-focus sealed tube
Oxford Diffraction, Enhance ULTRA assembly monochromator
Detector resolution: 8.1241 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2006)

T_{min} = 0.594, T_{max} = 1.000
3831 measured reflections
1981 independent reflections
1883 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 61.6°, θ_{min} = 5.5°
h = −11→6
k = −14→12
l = −9→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.091
S = 1.09
1981 reflections
161 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.6835P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0042 (10)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
Cl	0.72704 (5)	0.40149 (4)	0.00302 (4)	0.0364 (2)
N1	0.62280 (14)	0.24302 (12)	0.79789 (14)	0.0306 (4)
H14	0.6564	0.2871	0.8558	0.037*
N2	0.48201 (14)	0.15944 (11)	0.67424 (13)	0.0284 (4)
H15	0.4056	0.1383	0.6354	0.034*
C1	0.69789 (19)	0.17205 (15)	0.73092 (18)	0.0345 (4)
H1	0.7937	0.1622	0.7383	0.041*
C2	0.60936 (18)	0.11937 (15)	0.65322 (17)	0.0325 (4)
H2	0.6305	0.0651	0.5951	0.039*
C3	0.49175 (17)	0.23477 (13)	0.76179 (15)	0.0263 (4)
C4	0.37597 (17)	0.29425 (14)	0.81497 (16)	0.0274 (4)

H4	0.4159	0.3502	0.8723	0.033*
C5	0.29045 (19)	0.34994 (15)	0.70929 (18)	0.0330 (4)
H51	0.3418	0.4108	0.6771	0.040*
H52	0.2720	0.3004	0.6378	0.040*
C6	0.15650 (19)	0.38812 (15)	0.75959 (19)	0.0357 (5)
H61	0.1051	0.4282	0.6925	0.043*
H62	0.1749	0.4359	0.8328	0.043*
C7	0.07197 (19)	0.29466 (16)	0.80081 (19)	0.0377 (5)
H71	−0.0086	0.3211	0.8440	0.045*
H72	0.0389	0.2549	0.7246	0.045*
C8	0.15091 (18)	0.22119 (14)	0.88886 (17)	0.0300 (4)
C9	0.29331 (18)	0.22005 (13)	0.89655 (16)	0.0275 (4)
C10	0.3616 (2)	0.15248 (16)	0.98209 (17)	0.0359 (5)
H10	0.4583	0.1524	0.9875	0.043*
C11	0.2911 (2)	0.08543 (17)	1.05936 (19)	0.0424 (5)
H11	0.3389	0.0398	1.1174	0.051*
C12	0.1495 (2)	0.08569 (16)	1.05108 (19)	0.0417 (5)
H12	0.0998	0.0399	1.1033	0.050*
C13	0.0822 (2)	0.15226 (16)	0.96731 (18)	0.0380 (5)
H13	−0.0146	0.1516	0.9623	0.046*
O	0.46819 (17)	0.45111 (15)	0.17630 (17)	0.0595 (5)
H16	0.415 (3)	0.487 (2)	0.125 (2)	0.089*
H17	0.539 (2)	0.435 (3)	0.136 (3)	0.089*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0348 (3)	0.0341 (3)	0.0390 (3)	−0.00069 (18)	−0.00995 (19)	0.00005 (18)
N1	0.0251 (8)	0.0341 (8)	0.0325 (8)	−0.0043 (6)	−0.0007 (6)	−0.0007 (7)
N2	0.0249 (8)	0.0308 (8)	0.0293 (8)	−0.0026 (6)	0.0009 (6)	−0.0017 (6)
C1	0.0259 (9)	0.0394 (10)	0.0384 (10)	0.0039 (8)	0.0045 (8)	0.0050 (9)
C2	0.0321 (10)	0.0330 (10)	0.0331 (10)	0.0061 (8)	0.0075 (8)	0.0021 (8)
C3	0.0262 (9)	0.0269 (9)	0.0259 (9)	−0.0048 (7)	0.0021 (7)	0.0025 (7)
C4	0.0253 (9)	0.0277 (9)	0.0294 (9)	−0.0031 (7)	0.0033 (7)	−0.0049 (7)
C5	0.0328 (10)	0.0299 (10)	0.0362 (10)	0.0012 (8)	0.0028 (8)	0.0013 (8)
C6	0.0330 (10)	0.0319 (10)	0.0419 (11)	0.0049 (8)	−0.0007 (8)	−0.0060 (8)
C7	0.0268 (9)	0.0419 (11)	0.0444 (11)	−0.0005 (8)	0.0021 (8)	−0.0083 (9)
C8	0.0289 (9)	0.0311 (9)	0.0306 (9)	−0.0048 (8)	0.0060 (7)	−0.0111 (8)
C9	0.0295 (9)	0.0283 (9)	0.0251 (9)	−0.0033 (7)	0.0046 (7)	−0.0065 (7)
C10	0.0324 (10)	0.0438 (11)	0.0318 (10)	−0.0018 (8)	0.0042 (8)	0.0012 (9)
C11	0.0528 (13)	0.0426 (12)	0.0323 (10)	−0.0025 (10)	0.0054 (9)	0.0043 (9)
C12	0.0505 (13)	0.0408 (11)	0.0351 (11)	−0.0170 (10)	0.0143 (9)	−0.0056 (9)
C13	0.0331 (10)	0.0427 (11)	0.0388 (11)	−0.0110 (9)	0.0098 (8)	−0.0126 (9)
O	0.0457 (10)	0.0654 (11)	0.0674 (11)	0.0046 (8)	0.0037 (8)	0.0186 (9)

Geometric parameters (Å, º)

N1—C3	1.330 (2)	C6—H61	0.9900
N1—C1	1.378 (2)	C6—H62	0.9900
N1—H14	0.8800	C7—C8	1.504 (3)
N2—C3	1.328 (2)	C7—H71	0.9900
N2—C2	1.378 (2)	C7—H72	0.9900
N2—H15	0.8800	C8—C13	1.398 (3)
C1—C2	1.344 (3)	C8—C9	1.398 (3)
C1—H1	0.9500	C9—C10	1.392 (3)
C2—H2	0.9500	C10—C11	1.384 (3)
C3—C4	1.495 (2)	C10—H10	0.9500
C4—C9	1.532 (2)	C11—C12	1.390 (3)
C4—C5	1.535 (3)	C11—H11	0.9500
C4—H4	1.0000	C12—C13	1.369 (3)
C5—C6	1.521 (3)	C12—H12	0.9500
C5—H51	0.9900	C13—H13	0.9500
C5—H52	0.9900	O—H16	0.862 (10)
C6—C7	1.521 (3)	O—H17	0.861 (10)
C3—N1—C1	109.69 (15)	C7—C6—H61	109.6
C3—N1—H14	125.2	C5—C6—H62	109.6
C1—N1—H14	125.2	C7—C6—H62	109.6
C3—N2—C2	109.86 (15)	H61—C6—H62	108.1
C3—N2—H15	125.1	C8—C7—C6	112.62 (15)
C2—N2—H15	125.1	C8—C7—H71	109.1
C2—C1—N1	106.78 (16)	C6—C7—H71	109.1
C2—C1—H1	126.6	C8—C7—H72	109.1
N1—C1—H1	126.6	C6—C7—H72	109.1
C1—C2—N2	106.64 (16)	H71—C7—H72	107.8
C1—C2—H2	126.7	C13—C8—C9	117.99 (18)
N2—C2—H2	126.7	C13—C8—C7	120.10 (17)
N2—C3—N1	107.02 (15)	C9—C8—C7	121.90 (16)
N2—C3—C4	126.23 (15)	C10—C9—C8	119.65 (16)
N1—C3—C4	126.66 (15)	C10—C9—C4	119.22 (15)
C3—C4—C9	109.51 (14)	C8—C9—C4	121.11 (16)
C3—C4—C5	111.11 (14)	C11—C10—C9	121.25 (18)
C9—C4—C5	113.71 (14)	C11—C10—H10	119.4
C3—C4—H4	107.4	C9—C10—H10	119.4
C9—C4—H4	107.4	C10—C11—C12	119.2 (2)
C5—C4—H4	107.4	C10—C11—H11	120.4
C6—C5—C4	110.30 (15)	C12—C11—H11	120.4
C6—C5—H51	109.6	C13—C12—C11	119.65 (18)
C4—C5—H51	109.6	C13—C12—H12	120.2
C6—C5—H52	109.6	C11—C12—H12	120.2
C4—C5—H52	109.6	C12—C13—C8	122.23 (18)
H51—C5—H52	108.1	C12—C13—H13	118.9
C5—C6—C7	110.20 (15)	C8—C13—H13	118.9

C5—C6—H61	109.6	H16—O—H17	107 (3)
C3—N1—C1—C2	−0.4 (2)	C6—C7—C8—C9	−19.8 (2)
N1—C1—C2—N2	0.1 (2)	C13—C8—C9—C10	−0.9 (2)
C3—N2—C2—C1	0.2 (2)	C7—C8—C9—C10	178.28 (16)
C2—N2—C3—N1	−0.50 (19)	C13—C8—C9—C4	−179.19 (15)
C2—N2—C3—C4	−177.17 (16)	C7—C8—C9—C4	0.0 (2)
C1—N1—C3—N2	0.56 (19)	C3—C4—C9—C10	44.9 (2)
C1—N1—C3—C4	177.21 (16)	C5—C4—C9—C10	169.90 (16)
N2—C3—C4—C9	69.1 (2)	C3—C4—C9—C8	−136.78 (16)
N1—C3—C4—C9	−106.93 (19)	C5—C4—C9—C8	−11.8 (2)
N2—C3—C4—C5	−57.3 (2)	C8—C9—C10—C11	0.5 (3)
N1—C3—C4—C5	126.63 (18)	C4—C9—C10—C11	178.83 (17)
C3—C4—C5—C6	166.88 (15)	C9—C10—C11—C12	0.1 (3)
C9—C4—C5—C6	42.8 (2)	C10—C11—C12—C13	−0.2 (3)
C4—C5—C6—C7	−63.2 (2)	C11—C12—C13—C8	−0.2 (3)
C5—C6—C7—C8	51.0 (2)	C9—C8—C13—C12	0.8 (3)
C6—C7—C8—C13	159.38 (16)	C7—C8—C13—C12	−178.46 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H14···Cl^{i}	0.88	2.21	3.0897 (16)	176
N2—H15···Cl^{ii}	0.88	2.25	3.1164 (15)	169
O—H17···Cl	0.86 (1)	2.41 (1)	3.2612 (18)	173 (3)
O—H16···Cl^{iii}	0.86 (1)	2.37 (1)	3.2252 (17)	175 (3)

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