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1-Allyl-2,3-cyclopentenopyridinium chloride

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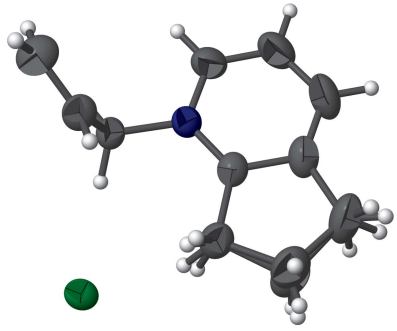
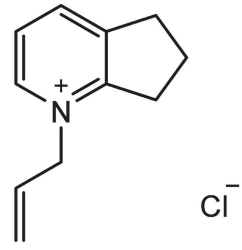
The title compound, $C_{11}H_{14}N^{+}\cdot Cl^{-}$, was obtained by reaction of 2,3-cyclopentenopyridine and allyl chloride. A network of weak C—H···Cl hydrogen bonds is observed in the crystal structure.

3D view



Chemical scheme



Structure description

The title compound has been prepared in a continuation of our interest in chloride-based ionic liquids as solvents for cellulose (Bentivoglio *et al.*, 2006; Wang *et al.*, 2012; Liu *et al.*, 2016). The reactions of cycloalkenopyridines have been reviewed by Beschke (1978). Related structures of 2,3-cyclopentenopyridinium salts are rare (Ammon & Jensen, 1966; Albov *et al.*, 2004). A similar 1-allylpyridinium chloride has been reported recently (Bentivoglio *et al.*, 2017).

In the title compound, the allyl group is twisted out of the plane of the heterocyclic ring by 84°.. The cyclopentene ring adopts a typical envelope conformation. The two possible conformations of the envelope are mirrored in the two components of positional disorder. The components C3 and C3*A* are located out of the C1/C2–C5 plane by 0.28 (1) and 0.25 (3) Å, respectively, a with a final occupancy ratio of 0.71 (2):0.29 (2).

In the crystal, weak C—H···Cl hydrogen bonds (Fig. 1, Table 1) create a network in which the chloride ions are fivefold coordinated by the pyridinium cations (Fig. 2).

Synthesis and crystallization

A solution of freshly distilled 2,3-cyclopentenopyridine (5.0 g, 42.0 mmol) and allyl chloride (6.4 g, 83.6 mmol) in CH_3CN (5 ml) was refluxed for 48 h. The product was precipitated by the addition of Et_2O (100 ml), kept in the freezer overnight, then filtered off, washed with Et_2O, and dried *in vacuo* yielding 7.6 g (92%) of a deliquescent powder. A solution of the crude product in CH_2Cl_2 was treated with charcoal to give a grey solid,

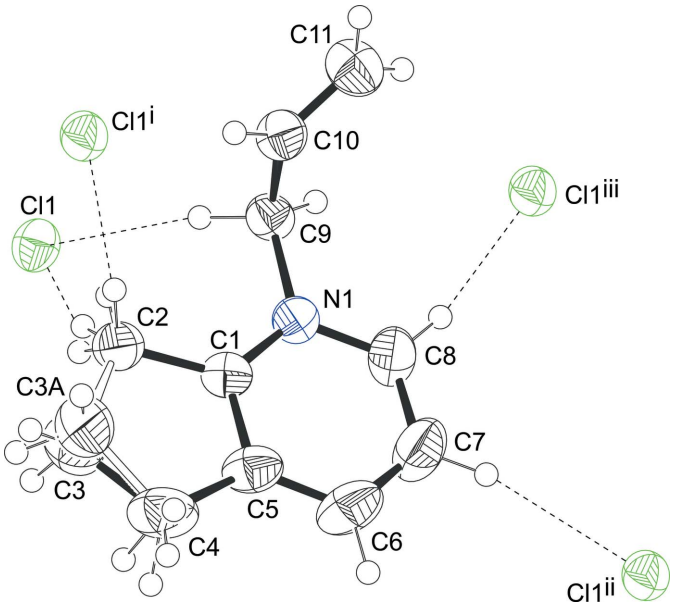


Figure 1
The molecular structure of the title compound, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. The minor-disorder component is represented by open bonds. C—H···Cl hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

which was further purified by slow evaporation of a CH_2Cl_2/EtOAc (2:1) solution. After removal of an initial blackish precipitate, colourless crystals separated from the filtrate, m.p. 427 K.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.12 (*dd*, J = 6.2, 1.2 Hz, 1H), 8.48 (*dd*, J = 7.8, 1.2 Hz, 1H), 7.95 (*dd*, J = 7.8, 6.2 Hz, 1H), 6.11 (*ddt*, J = 16.4, 10.3, 5.9 Hz, 1H), 5.48–5.24 (*m*, 4H), 3.40 (*t*, J = 7.7 Hz, 2H), 3.12 (*t*, J = 7.6 Hz, 2H), 2.18 (*quin*, J = 7.8 Hz, 2H) p.p.m. ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.1, 144.8, 142.0, 140.9, 130.7, 125.6, 120.7, 59.5, 31.2, 30.5, 22.0 p.p.m. IR (neat): ν 3382, 2965, 2898, 2830, 1617, 1489, 1467, 1430, 1340, 1290, 1207, 1011, 958, 822, 739 cm^{-1}.

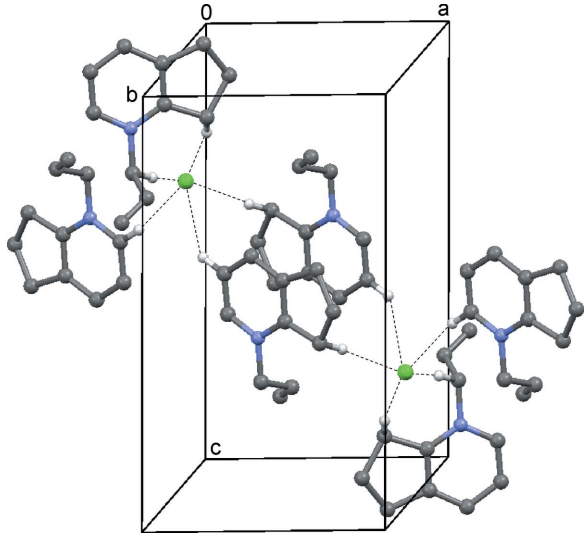


Figure 2
Fivefold-coordinated chloride ions in the unit cell of the title compound. Only H atoms involved in contacts are shown.

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···Cl1	0.98	2.80	3.748 (2)	164
C9—H9A···Cl1	0.98	2.64	3.584 (2)	163
C2—H2B···Cl1^{i}	0.98	2.67	3.643 (2)	175
C7—H7···Cl1^{ii}	0.94	2.75	3.545 (2)	143
C8—H8···Cl1^{iii}	0.94	2.59	3.510 (2)	166

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{14}N^+\cdot Cl^-$
M_r	195.68
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	233
a, b, c (Å)	8.1093 (3), 9.1624 (5), 14.6575 (7)
β (°)	94.241 (3)
V (Å^3)	1086.08 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.31
Crystal size (mm)	0.28 × 0.16 × 0.11
Data collection	
Diffractometer	Nonius KappaCCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6048, 1905, 1617
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.092, 1.05
No. of reflections	1906
No. of parameters	140
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, −0.15

Computer programs: *COLLECT* (Hooft, 1998), *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The disordered cyclopentene ring was refined using six geometrical restraints (SADI) for chemically equivalent, corresponding 1,2- and 1,3-distances in the two disorder components. The disordered C3 and C3*A* positions were both refined anisotropically, and their final relative occupancies were 0.71 (2) and 0.29 (2).

References

Albov, D. V., Rybakov, V. B., Babaev, E. V. & Aslanov, L. A. (2004). *Acta Cryst.* E**60**, o2313–o2314.
Ammon, H. L. & Jensen, L. H. (1966). *J. Am. Chem. Soc.* **88**, 681–688.

Bentivoglio, G., Laus, G., Kahlenberg, V., Röder, T. & Schottenberger, H. (2017). *IUCrData*, **2**, x170598.
Bentivoglio, G., Röder, T., Fasching, M., Buchberger, M., Schottenberger, H. & Sixta, H. (2006). *Lenzinger Ber.* **86**, 154–161.
Beschke, H. (1978). *Aldrichim. Acta*, **11**, 13–16.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Liu, Y.-R., Thomsen, K., Nie, Y., Zhang, S.-J. & Meyer, A. S. (2016). *Green Chem.* **18**, 6246–6254.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Wang, H., Gurau, G. & Rogers, R. D. (2012). *Chem. Soc. Rev.* **41**, 1519–1537.

full crystallographic data

IUCrData (2017). **2**, x170669 [https://doi.org/10.1107/S2414314617006691]

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Crystal data

$C_{11}H_{14}N^+\cdot Cl^-$
M_r = 195.68
Monoclinic, $P2_1/n$
a = 8.1093 (3) Å
b = 9.1624 (5) Å
c = 14.6575 (7) Å
β = 94.241 (3)°
V = 1086.08 (9) Å^3
Z = 4
$F(000)$ = 416
D_x = 1.197 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8675 reflections
θ = 1.0–25.0°
μ = 0.31 mm^{-1}
T = 233 K
Prism, colourless
0.28 × 0.16 × 0.11 mm

Data collection

Nonius KappaCCD diffractometer
Detector resolution: 9.6 pixels mm^{-1}
phi– and ω–scans
6048 measured reflections
1905 independent reflections
1617 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.0°, θ_{min} = 2.6°
h = −9→9
k = −10→10
l = −17→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.092
S = 1.05
1906 reflections
140 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.2786P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

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}	Occ. (<1)
Cl1	0.03447 (5)	0.44823 (5)	0.28693 (3)	0.04502 (17)	
N1	−0.10204 (15)	0.79887 (14)	0.10639 (9)	0.0386 (3)	
C1	0.02285 (19)	0.74677 (18)	0.06053 (11)	0.0394 (4)	
C2	0.1815 (2)	0.6849 (2)	0.10083 (13)	0.0488 (5)	
H2A	0.1623	0.6094	0.1462	0.059*	0.71 (2)
H2B	0.2524	0.7611	0.1296	0.059*	0.71 (2)
H2C	0.153 (8)	0.584 (8)	0.129 (5)	0.059*	0.29 (2)
H2D	0.217 (9)	0.716 (9)	0.140 (5)	0.059*	0.29 (2)
C4	0.1684 (3)	0.6863 (3)	−0.06749 (15)	0.0723 (7)	
H4A	0.2347	0.7640	−0.0926	0.087*	0.71 (2)
H4B	0.1445	0.6120	−0.1147	0.087*	0.71 (2)
H4C	0.196 (11)	0.700 (10)	−0.116 (6)	0.087*	0.29 (2)
H4D	0.140 (11)	0.567 (10)	−0.075 (6)	0.087*	0.29 (2)
C5	0.0123 (2)	0.7463 (2)	−0.03423 (12)	0.0517 (5)	
C6	−0.1289 (3)	0.7974 (3)	−0.08175 (13)	0.0665 (6)	
H6	−0.1391	0.7956	−0.1460	0.080*	
C7	−0.2548 (3)	0.8511 (3)	−0.03341 (14)	0.0668 (6)	
H7	−0.3515	0.8873	−0.0648	0.080*	
C8	−0.2398 (2)	0.8519 (2)	0.05995 (13)	0.0534 (5)	
H8	−0.3259	0.8898	0.0924	0.064*	
C9	−0.0906 (2)	0.80459 (18)	0.20819 (10)	0.0407 (4)	
H9A	−0.0333	0.7173	0.2327	0.049*	
H9B	−0.2022	0.8049	0.2297	0.049*	
C10	0.0005 (2)	0.93774 (19)	0.24313 (12)	0.0457 (4)	
H10	0.1149	0.9443	0.2372	0.055*	
C11	−0.0739 (2)	1.0444 (2)	0.28143 (14)	0.0563 (5)	
H11A	−0.1883	1.0393	0.2879	0.068*	
H11B	−0.0135	1.1267	0.3027	0.068*	
C3	0.2577 (9)	0.6200 (9)	0.0171 (3)	0.0669 (18)	0.71 (2)
H3A	0.3759	0.6428	0.0191	0.080*	0.71 (2)
H3B	0.2446	0.5136	0.0164	0.080*	0.71 (2)
C3A	0.2852 (12)	0.672 (3)	0.0183 (4)	0.068 (5)	0.29 (2)
H3A1	0.3687	0.7497	0.0200	0.082*	0.29 (2)
H3A2	0.3419	0.5777	0.0190	0.082*	0.29 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0394 (3)	0.0451 (3)	0.0500 (3)	−0.00190 (17)	0.00033 (18)	0.00391 (18)
N1	0.0414 (7)	0.0383 (7)	0.0366 (7)	−0.0004 (6)	0.0058 (6)	0.0037 (6)
C1	0.0391 (8)	0.0408 (9)	0.0388 (9)	−0.0073 (7)	0.0058 (7)	−0.0021 (7)
C2	0.0409 (10)	0.0592 (13)	0.0463 (11)	0.0019 (8)	0.0032 (8)	−0.0069 (9)
C4	0.0610 (13)	0.108 (2)	0.0496 (12)	−0.0036 (13)	0.0160 (10)	−0.0213 (13)
C5	0.0518 (10)	0.0659 (12)	0.0379 (9)	−0.0095 (9)	0.0068 (8)	−0.0041 (8)
C6	0.0705 (13)	0.0918 (16)	0.0364 (10)	−0.0073 (12)	−0.0016 (9)	0.0086 (10)

C7	0.0595 (12)	0.0861 (16)	0.0536 (12)	0.0114 (11)	−0.0045 (10)	0.0169 (11)
C8	0.0473 (10)	0.0590 (12)	0.0540 (11)	0.0100 (9)	0.0049 (8)	0.0103 (9)
C9	0.0473 (9)	0.0402 (9)	0.0354 (9)	0.0019 (7)	0.0091 (7)	0.0028 (7)
C10	0.0371 (9)	0.0547 (11)	0.0456 (10)	−0.0013 (8)	0.0057 (7)	−0.0010 (8)
C11	0.0509 (10)	0.0498 (11)	0.0689 (13)	−0.0064 (9)	0.0092 (9)	−0.0076 (9)
C3	0.062 (3)	0.074 (4)	0.067 (3)	0.009 (2)	0.0206 (18)	−0.0084 (18)
C3A	0.050 (6)	0.092 (13)	0.064 (7)	0.011 (6)	0.017 (4)	−0.004 (5)

Geometric parameters (Å, º)

N1—C1	1.344 (2)	C5—C6	1.377 (3)
N1—C8	1.355 (2)	C6—C7	1.376 (3)
N1—C9	1.489 (2)	C6—H6	0.9400
C1—C5	1.385 (2)	C7—C8	1.365 (3)
C1—C2	1.487 (2)	C7—H7	0.9400
C2—C3A	1.527 (7)	C8—H8	0.9400
C2—C3	1.534 (4)	C9—C10	1.497 (2)
C2—H2A	0.9800	C9—H9A	0.9800
C2—H2B	0.9800	C9—H9B	0.9800
C2—H2C	1.05 (8)	C10—C11	1.298 (3)
C2—H2D	0.69 (7)	C10—H10	0.9400
C4—C5	1.495 (3)	C11—H11A	0.9400
C4—C3	1.516 (5)	C11—H11B	0.9400
C4—C3A	1.523 (7)	C3—H3A	0.9800
C4—H4A	0.9800	C3—H3B	0.9800
C4—H4B	0.9800	C3A—H3A1	0.9800
C4—H4C	0.78 (9)	C3A—H3A2	0.9800
C4—H4D	1.12 (9)		
C1—N1—C8	120.00 (15)	C7—C6—C5	118.78 (18)
C1—N1—C9	121.34 (13)	C7—C6—H6	120.6
C8—N1—C9	118.62 (14)	C5—C6—H6	120.6
N1—C1—C5	120.63 (15)	C8—C7—C6	120.28 (19)
N1—C1—C2	126.75 (15)	C8—C7—H7	119.9
C5—C1—C2	112.62 (15)	C6—C7—H7	119.9
C1—C2—C3A	103.0 (4)	N1—C8—C7	120.71 (17)
C1—C2—C3	102.6 (2)	N1—C8—H8	119.6
C1—C2—H2A	111.2	C7—C8—H8	119.6
C3—C2—H2A	111.2	N1—C9—C10	111.36 (13)
C1—C2—H2B	111.2	N1—C9—H9A	109.4
C3—C2—H2B	111.2	C10—C9—H9A	109.4
H2A—C2—H2B	109.2	N1—C9—H9B	109.4
C1—C2—H2C	106 (4)	C10—C9—H9B	109.4
C3A—C2—H2C	113 (4)	H9A—C9—H9B	108.0
C1—C2—H2D	118 (7)	C11—C10—C9	121.86 (16)
C3A—C2—H2D	118 (7)	C11—C10—H10	119.1
H2C—C2—H2D	97 (7)	C9—C10—H10	119.1
C5—C4—C3	104.2 (2)	C10—C11—H11A	120.0

C5—C4—C3A	104.6 (4)	C10—C11—H11B	120.0
C5—C4—H4A	110.9	H11A—C11—H11B	120.0
C3—C4—H4A	110.9	C4—C3—C2	107.6 (3)
C5—C4—H4B	110.9	C4—C3—H3A	110.2
C3—C4—H4B	110.9	C2—C3—H3A	110.2
H4A—C4—H4B	108.9	C4—C3—H3B	110.2
C5—C4—H4C	123 (7)	C2—C3—H3B	110.2
C3A—C4—H4C	125 (7)	H3A—C3—H3B	108.5
C5—C4—H4D	103 (4)	C4—C3A—C2	107.6 (6)
C3A—C4—H4D	96 (4)	C4—C3A—H3A1	110.2
H4C—C4—H4D	98 (8)	C2—C3A—H3A1	110.2
C6—C5—C1	119.57 (18)	C4—C3A—H3A2	110.2
C6—C5—C4	130.74 (18)	C2—C3A—H3A2	110.2
C1—C5—C4	109.68 (17)	H3A1—C3A—H3A2	108.5
C8—N1—C1—C5	−0.2 (2)	C3A—C4—C5—C1	−8.5 (11)
C9—N1—C1—C5	−178.01 (15)	C1—C5—C6—C7	1.6 (3)
C8—N1—C1—C2	−179.96 (18)	C4—C5—C6—C7	−178.2 (2)
C9—N1—C1—C2	2.2 (2)	C5—C6—C7—C8	−0.7 (3)
N1—C1—C2—C3A	−169.5 (11)	C1—N1—C8—C7	1.1 (3)
C5—C1—C2—C3A	10.7 (11)	C9—N1—C8—C7	179.00 (18)
N1—C1—C2—C3	170.1 (4)	C6—C7—C8—N1	−0.7 (3)
C5—C1—C2—C3	−9.7 (4)	C1—N1—C9—C10	82.79 (18)
N1—C1—C5—C6	−1.2 (3)	C8—N1—C9—C10	−95.10 (18)
C2—C1—C5—C6	178.66 (18)	N1—C9—C10—C11	110.0 (2)
N1—C1—C5—C4	178.66 (17)	C5—C4—C3—C2	−18.0 (7)
C2—C1—C5—C4	−1.5 (2)	C1—C2—C3—C4	16.9 (6)
C3—C4—C5—C6	−168.0 (4)	C5—C4—C3A—C2	14.9 (17)
C3A—C4—C5—C6	171.4 (11)	C1—C2—C3A—C4	−15.5 (17)
C3—C4—C5—C1	12.2 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···Cl1	0.98	2.80	3.748 (2)	164
C9—H9*A*···Cl1	0.98	2.64	3.584 (2)	163
C2—H2*B*···Cl1^{i}	0.98	2.67	3.643 (2)	175
C7—H7···Cl1^{ii}	0.94	2.75	3.545 (2)	143
C8—H8···Cl1^{iii}	0.94	2.59	3.510 (2)	166

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