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Dichloridobis(4-fluoroaniline-κN)zinc

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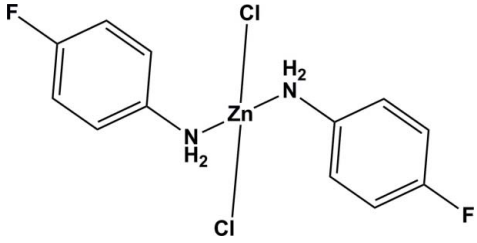
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.020; wR factor = 0.043; data-to-parameter ratio = 15.2.

In the title compound, $[ZnCl_2(C_6H_6FN)_2]$, the Zn^{II} atom has a slightly distorted tetrahedral geometry, being coordinated by the N atoms of two 4-fluoroaniline molecules and the two Cl^- anions. The two benzene rings are almost perpendicular to one another, making a dihedral angle of 89.96 (13)°. In the crystal, molecules are linked *via* pairs of N—H···Cl hydrogen bonds, forming chains propagating along the *b* axis. These chains are in turn linked *via* a second pair of N—H···Cl hydrogen bonds, forming a two-dimensional network parallel to the *ab* plane. The title compound crystallizes in the space group $Pca2_1$ and exhibits weak second harmonic generation (SHG) properties.

Related literature

For the measurement of second harmonic generation (SHG) conversion efficiency, see: Kurtz & Perry (1968). For the crystal structure of dichlorido-bis(*p*-chloroaniline)zinc, see: Subashini *et al.* (2012*a*) and for the crystal structure of dichlorodo-bis(*p*-bromoaniline)zinc, see: Subashini *et al.* (2012*b*); Feng *et al.* (2003).



Experimental

Crystal data

$[ZnCl_2(C_6H_6FN)_2]$
M_r = 358.51
Orthorhombic, $Pca2_1$
a = 11.6817 (5) Å
b = 4.7080 (2) Å
c = 25.2056 (15) Å
V = 1386.24 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.17 mm^{-1}
T = 173 K
0.45 × 0.22 × 0.10 mm

Data collection

Stoe IPDS 2 diffractometer
Absorption correction: multi-scan (*MULscanABS* in *PLATON*; Spek, 2009)
T_{min} = 0.742, T_{max} = 0.805
7963 measured reflections
2613 independent reflections
2465 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.043
S = 1.02
2613 reflections
172 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Absolute structure: Flack (1983), 1273 Friedel pairs
Flack parameter: 0.013 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···Cl2^{i}	0.92	2.63	3.436 (2)	147
N2—H2B···Cl1^{i}	0.92	2.55	3.380 (2)	151
N1—H1A···Cl2^{ii}	0.92	2.59	3.479 (2)	162
N2—H2A···Cl1^{iii}	0.92	2.55	3.439 (2)	162

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

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*, *PLATON* and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5178).

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supporting information

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Dichloridobis(4-fluoroaniline-κN)zinc

Ashokkumar Subashini, Kandasamy Ramamurthi and Helen Stoeckli-Evans

S1. Comment

In our search for compounds exhibiting second harmonic generation (SHG) properties we have synthesized a series of $ZnCl_2$ complexes of *p*-halogen substituted anilines. The title compound, the $ZnCl_2$ complex of *p*-fluoroaniline crystallized in the noncentrosymmetric orthorhombic space group $Pca2_1$, while the *p*-chloroaniline (Subashini *et al.*, 2012*a*) and *p*-bromoaniline (Subashini *et al.*, 2012*b*; Feng *et al.*, 2003) $ZnCl_2$ complexes crystallized in the centrosymmetric monoclinic space group *C*2/*c* and both molecules have crystallographic 2-fold rotation symmetry.

In the title compound (Fig. 1), the zinc atom has a slightly distorted tetrahedral geometry, being coordinated by the atoms N1 and N2 of two *p*-fluoroaniline molecules and the two Cl^- anions. The two benzene rings (C1—C6 and C7—C12) are perpendicular to one another with a dihedral angle of 89.96 (13)°. In the *p*-chloroaniline and *p*-bromoaniline $ZnCl_2$ complexes mentioned above the same angles are 80.65 (16) and 80.0 (3)°, respectively.

In the crystal of the title compound, molecules are linked *via* a pair of N—H···Cl hydrogen bonds forming chains propagating along the *b* axis direction. These chains are in turn linked *via* a second pair of N—H···Cl hydrogen bonds to form a two-dimensional network lying parallel to the *ab* plane (Table 1 and Fig. 2). This contrasts with the packing in the crystals of the *p*-chloroaniline and *p*-bromoaniline $ZnCl_2$ complexes. There molecules are linked by four N—H···halogen bonds to form chains propagating along [010], with no significant interactions between the chains.

As the title compound crystallized in a noncentrosymmetric space group it was decided to measure the second harmonic generation (SHG) properties of all three compounds; dichloro-bis(*p*-fluoroaniline)zinc, dichloro-bis(*p*-chloroaniline)zinc and dichloro-bis(*p*-bromoaniline)zinc. The SHG conversion efficiency was determined by the powder technique developed by (Kurtz & Perry, 1968). The crystals were powdered and the fine powdered samples were inserted in a micro-capillary tube and then subjected to a Q-switched Nd: YAG laser emitting 1064 nm radiation with 3.9 mJ/pulse. The frequency doubling was confirmed by the emission of green radiation of wavelength 532 nm collected by a monochromator after separating the 1064 nm pump beam with an IR-blocking filter. A detector connected to a power meter was used to detect the second harmonic intensity.

The output beam voltage produced by dichloro-bis(*p*-fluoroaniline)zinc, dichloro-bis(*p*-chloroaniline)zinc and dichloro-bis(*p*-bromoaniline)zinc derivatives were 15, 3 and 10 mV, respectively. The same quantity of crystalline KDP (potassium dihydrogen phosphate) powder, used as a reference material, produced 140 mV as output beam voltage. Hence the three samples exhibits SHG efficiency of only *ca* 0.11, 0.02 and 0.07 times that of the KDP.

S2. Experimental

The title compound was prepared by the condensation reaction of *p*-fluoroaniline with $ZnCl_2$ in a 1:1 molar ratio. The reaction mixture was dissolved in methanol and heated under reflux for 6 h. The resulting solution was filtered and allowed to evaporate. Colourless rod-like crystals of the title compound, suitable for X-ray diffraction analysis, were obtained in a period of *ca* 7 days. The same method was used for the preparation of the *p*-chloroaniline and *p*-bromo-

aniline $ZnCl_2$ complexes.

S3. Refinement

All the H atoms could be located in a difference Fourier map. In the final cycles of refinement they were included in calculated positions and treated as riding atoms: N—H = 0.92 Å and C—H = 0.95 Å with U_{iso}(H) = 1.2U_{eq}(N or C).

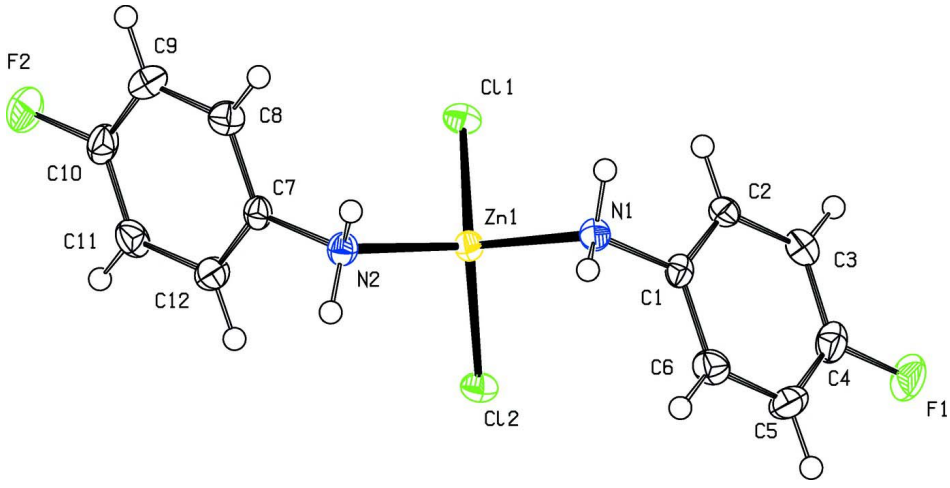

Figure 1

A view of the molecular structure of the title compound with the atom numbering. The displacement ellipsoids are drawn at the 50% probability level.

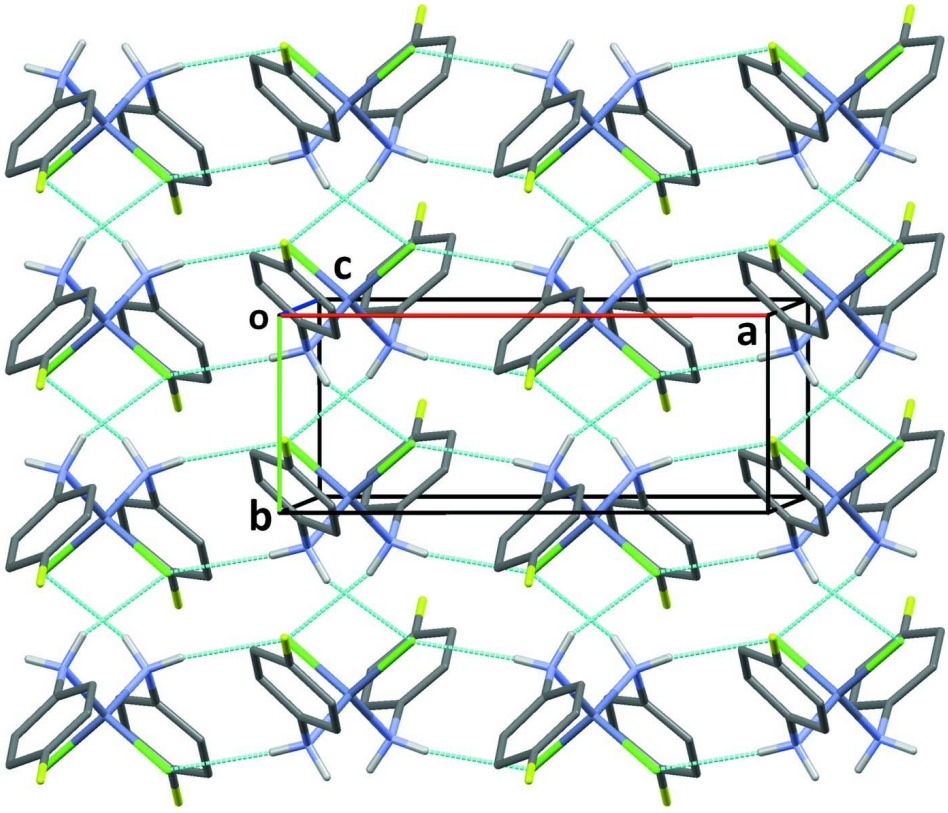

Figure 2

A view along the *c* axis of the crystal packing of the title compound. The N—H···Cl hydrogen bonds are shown as dashed cyan lines (see Table 1 for details).

Dichloridobis(4-fluoroaniline-*κN*)zinc

Crystal data

$[ZnCl_2(C_6H_6FN)_2]$
M_r = 358.51
Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
a = 11.6817 (5) Å
b = 4.7080 (2) Å
c = 25.2056 (15) Å
V = 1386.24 (12) Å^3
Z = 4
$F(000)$ = 720
D_x = 1.718 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 10039 reflections
θ = 1.6–26.1°
μ = 2.17 mm^{-1}
T = 173 K
Rod, colourless
0.45 × 0.22 × 0.10 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
φ and ω scans
Absorption correction: multi-scan (MULscanABS in *PLATON*; Spek, 2009)
T_{min} = 0.742, T_{max} = 0.805
7963 measured reflections
2613 independent reflections
2465 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.6°, θ_{min} = 1.6°
h = −14→12
k = −5→5
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.043$
$S = 1.02$
2613 reflections
172 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Absolute structure: Flack (1983), 1273 Friedel pairs
Absolute structure parameter: 0.013 (10)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.11820 (2)	0.94853 (5)	0.29991 (2)	0.0175 (1)
Cl1	0.24924 (5)	0.67311 (13)	0.25893 (2)	0.0231 (2)
Cl2	−0.01369 (5)	0.66951 (13)	0.33956 (2)	0.0224 (2)
F1	0.24874 (17)	0.4882 (4)	0.53656 (6)	0.0375 (5)
F2	0.00539 (17)	0.6379 (4)	0.05020 (6)	0.0386 (6)
N1	0.19821 (18)	1.1742 (4)	0.35892 (7)	0.0190 (6)
N2	0.03682 (17)	1.1921 (5)	0.24427 (7)	0.0193 (6)
C1	0.2140 (2)	1.0033 (5)	0.40640 (10)	0.0173 (8)
C2	0.3039 (2)	0.8160 (6)	0.40935 (9)	0.0206 (8)
C3	0.3164 (2)	0.6390 (6)	0.45336 (9)	0.0236 (8)
C4	0.2366 (2)	0.6601 (6)	0.49308 (9)	0.0267 (8)
C5	0.1466 (2)	0.8448 (7)	0.49146 (10)	0.0279 (8)
C6	0.1343 (2)	1.0192 (6)	0.44767 (12)	0.0247 (9)
C7	0.0273 (2)	1.0505 (5)	0.19283 (10)	0.0181 (7)
C8	0.1041 (2)	1.1133 (7)	0.15318 (10)	0.0242 (9)
C9	0.0976 (3)	0.9741 (7)	0.10479 (11)	0.0305 (9)
C10	0.0127 (2)	0.7762 (6)	0.09785 (9)	0.0263 (8)
C11	−0.0645 (2)	0.7084 (6)	0.13658 (10)	0.0258 (8)
C12	−0.0570 (2)	0.8484 (6)	0.18522 (9)	0.0236 (8)
H1A	0.26840	1.23560	0.34700	0.0230*
H1B	0.15510	1.33170	0.36710	0.0230*
H2	0.35790	0.80690	0.38120	0.0250*
H2A	−0.03540	1.23620	0.25630	0.0230*
H2B	0.07640	1.35950	0.24000	0.0230*
H3	0.37820	0.50830	0.45570	0.0280*
H5	0.09330	0.85340	0.51990	0.0340*
H6	0.07220	1.14880	0.44570	0.0300*
H8	0.16170	1.25240	0.15890	0.0290*

H9	0.15060	1.01470	0.07720	0.0370*
H11	−0.12190	0.56930	0.13050	0.0310*
H12	−0.10940	0.80520	0.21290	0.0280*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0174 (1)	0.0186 (1)	0.0167 (1)	−0.0009 (1)	−0.0010 (1)	−0.0002 (2)
Cl1	0.0180 (3)	0.0236 (3)	0.0277 (3)	0.0019 (3)	0.0033 (2)	−0.0017 (2)
Cl2	0.0187 (3)	0.0224 (3)	0.0261 (3)	−0.0031 (3)	0.0034 (2)	−0.0004 (2)
F1	0.0460 (9)	0.0433 (11)	0.0232 (8)	−0.0064 (9)	−0.0048 (9)	0.0147 (6)
F2	0.0423 (10)	0.0516 (13)	0.0218 (7)	0.0015 (9)	−0.0016 (6)	−0.0145 (7)
N1	0.0200 (10)	0.0179 (11)	0.0191 (9)	−0.0029 (9)	−0.0014 (8)	0.0020 (8)
N2	0.0215 (11)	0.0185 (11)	0.0180 (10)	0.0010 (10)	−0.0011 (8)	−0.0016 (8)
C1	0.0214 (13)	0.0145 (15)	0.0161 (13)	−0.0048 (10)	−0.0028 (10)	−0.0017 (8)
C2	0.0168 (12)	0.0252 (15)	0.0199 (12)	−0.0052 (11)	−0.0001 (9)	−0.0016 (10)
C3	0.0199 (13)	0.0231 (14)	0.0277 (13)	0.0009 (11)	−0.0043 (10)	−0.0005 (10)
C4	0.0335 (15)	0.0261 (14)	0.0204 (12)	−0.0074 (13)	−0.0050 (10)	0.0044 (10)
C5	0.0295 (14)	0.0329 (17)	0.0214 (12)	−0.0033 (14)	0.0073 (11)	0.0003 (12)
C6	0.0221 (15)	0.0241 (17)	0.0279 (15)	0.0057 (13)	0.0006 (11)	−0.0025 (10)
C7	0.0200 (12)	0.0171 (12)	0.0172 (12)	0.0035 (11)	−0.0028 (10)	0.0009 (10)
C8	0.0232 (14)	0.0240 (17)	0.0254 (14)	−0.0010 (13)	0.0010 (10)	−0.0001 (11)
C9	0.0298 (15)	0.040 (2)	0.0216 (13)	−0.0025 (14)	0.0068 (11)	0.0018 (11)
C10	0.0305 (14)	0.0306 (15)	0.0179 (12)	0.0081 (13)	−0.0026 (10)	−0.0057 (11)
C11	0.0213 (12)	0.0277 (16)	0.0284 (14)	−0.0025 (12)	−0.0050 (10)	−0.0069 (11)
C12	0.0241 (13)	0.0254 (14)	0.0212 (13)	0.0008 (12)	0.0021 (10)	0.0005 (10)

Geometric parameters (Å, º)

Zn1—Cl1	2.2565 (7)	C4—C5	1.365 (4)
Zn1—Cl2	2.2579 (7)	C5—C6	1.383 (4)
Zn1—N1	2.0530 (19)	C7—C8	1.375 (3)
Zn1—N2	2.046 (2)	C7—C12	1.383 (3)
F1—C4	1.370 (3)	C8—C9	1.387 (4)
F2—C10	1.369 (3)	C9—C10	1.372 (4)
N1—C1	1.454 (3)	C10—C11	1.367 (3)
N2—C7	1.462 (3)	C11—C12	1.395 (4)
N1—H1B	0.9200	C2—H2	0.9500
N1—H1A	0.9200	C3—H3	0.9500
N2—H2A	0.9200	C5—H5	0.9500
N2—H2B	0.9200	C6—H6	0.9500
C1—C6	1.398 (4)	C8—H8	0.9500
C1—C2	1.373 (3)	C9—H9	0.9500
C2—C3	1.395 (4)	C11—H11	0.9500
C3—C4	1.372 (3)	C12—H12	0.9500
Cl1—Zn1—Cl2	109.34 (2)	C1—C6—C5	119.5 (2)
Cl1—Zn1—N1	108.68 (6)	N2—C7—C12	119.4 (2)

Cl1—Zn1—N2	108.88 (6)	N2—C7—C8	119.8 (2)
Cl2—Zn1—N1	106.92 (6)	C8—C7—C12	120.8 (2)
Cl2—Zn1—N2	108.21 (6)	C7—C8—C9	120.1 (3)
N1—Zn1—N2	114.72 (8)	C8—C9—C10	118.2 (3)
Zn1—N1—C1	111.58 (14)	F2—C10—C11	118.3 (2)
Zn1—N2—C7	112.81 (16)	F2—C10—C9	118.7 (2)
C1—N1—H1A	109.00	C9—C10—C11	123.0 (2)
C1—N1—H1B	109.00	C10—C11—C12	118.4 (2)
H1A—N1—H1B	108.00	C7—C12—C11	119.5 (2)
Zn1—N1—H1B	109.00	C1—C2—H2	120.00
Zn1—N1—H1A	109.00	C3—C2—H2	120.00
Zn1—N2—H2B	109.00	C2—C3—H3	121.00
Zn1—N2—H2A	109.00	C4—C3—H3	121.00
H2A—N2—H2B	108.00	C4—C5—H5	121.00
C7—N2—H2A	109.00	C6—C5—H5	121.00
C7—N2—H2B	109.00	C1—C6—H6	120.00
N1—C1—C6	119.9 (2)	C5—C6—H6	120.00
N1—C1—C2	119.8 (2)	C7—C8—H8	120.00
C2—C1—C6	120.2 (2)	C9—C8—H8	120.00
C1—C2—C3	120.4 (2)	C8—C9—H9	121.00
C2—C3—C4	117.8 (2)	C10—C9—H9	121.00
C3—C4—C5	123.2 (2)	C10—C11—H11	121.00
F1—C4—C3	118.1 (2)	C12—C11—H11	121.00
F1—C4—C5	118.7 (2)	C7—C12—H12	120.00
C4—C5—C6	118.8 (2)	C11—C12—H12	120.00

Cl1—Zn1—N1—C1	−80.53 (15)	C2—C3—C4—F1	−179.6 (2)
Cl2—Zn1—N1—C1	37.40 (16)	C2—C3—C4—C5	−0.1 (4)
N2—Zn1—N1—C1	157.37 (14)	F1—C4—C5—C6	179.8 (2)
Cl1—Zn1—N2—C7	31.74 (16)	C3—C4—C5—C6	0.3 (4)
Cl2—Zn1—N2—C7	−87.00 (15)	C4—C5—C6—C1	−0.2 (4)
N1—Zn1—N2—C7	153.74 (15)	N2—C7—C8—C9	178.2 (3)
Zn1—N1—C1—C2	80.9 (2)	C12—C7—C8—C9	0.1 (4)
Zn1—N1—C1—C6	−95.7 (2)	N2—C7—C12—C11	−178.5 (2)
Zn1—N2—C7—C8	−98.8 (2)	C8—C7—C12—C11	−0.5 (4)
Zn1—N2—C7—C12	79.2 (2)	C7—C8—C9—C10	0.5 (4)
N1—C1—C2—C3	−176.3 (2)	C8—C9—C10—F2	179.9 (2)
C6—C1—C2—C3	0.3 (4)	C8—C9—C10—C11	−0.8 (5)
N1—C1—C6—C5	176.6 (2)	F2—C10—C11—C12	179.8 (2)
C2—C1—C6—C5	−0.1 (4)	C9—C10—C11—C12	0.5 (4)
C1—C2—C3—C4	−0.2 (4)	C10—C11—C12—C7	0.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···Cl2^{i}	0.92	2.63	3.436 (2)	147
N2—H2*B*···Cl1^{i}	0.92	2.55	3.380 (2)	151

N1—H1*A*···Cl2^{ii}	0.92	2.59	3.479 (2)	162
N2—H2*A*···Cl1^{iii}	0.92	2.55	3.439 (2)	162

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