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Crystal structure of dichloridobis(dimethyl *N*-cyanodithioiminocarbonate)zinc

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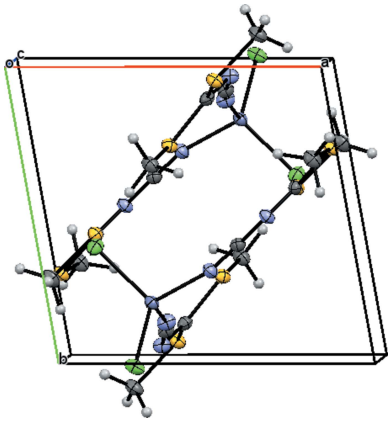
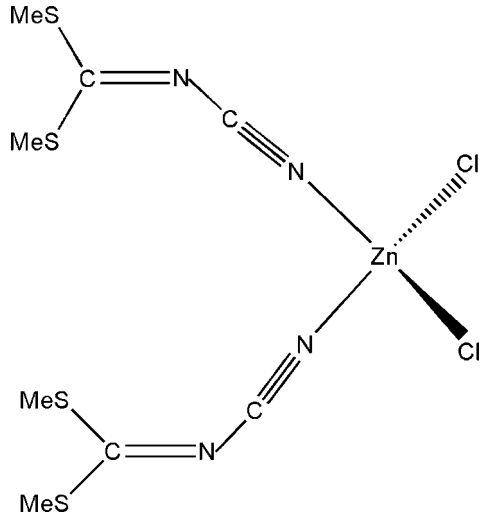
The Zn^{II} atom in the title complex, $[ZnCl_2(C_4H_6N_2S_2)_2]$, is coordinated in a distorted tetrahedral manner by two Cl atoms and two terminal N atoms of two dimethyl *N*-cyanodithioiminocarbonate ligands. In the crystal, the complex molecules are connected through C—H···Cl hydrogen bonds and Cl···S contacts, leading to a two-dimensional structure extending parallel to the *ab* plane.

1. Chemical context

Two N and two S atoms in dimethyl *N*-cyanodithioiminocarbonate (DMCDIC), which are expected to act as hard and soft donors, respectively, according to Pearson's concept, give an interesting coordination potential to this molecule. However, only one structure of a metal complex with DMCDIC acting as a ligand has been reported (Kojić-Prodić *et al.*, 1992). Very recently, we reported the crystal structure of $[CoCl_2(DMCDIC)_2]$ (Diop *et al.*, 2016). Because of the scarcity of data on the coordination ability of DMCDIC, we have focused on studying the interactions between some transition metal halides and this ligand, which has yielded the title complex.





2. Structural commentary

The structure of the title compound (Fig. 1) is isotypic with the Co complex reported recently (Diop *et al.*, 2016). The Zn^{II} atom is coordinated in a tetrahedral fashion by two Cl atoms

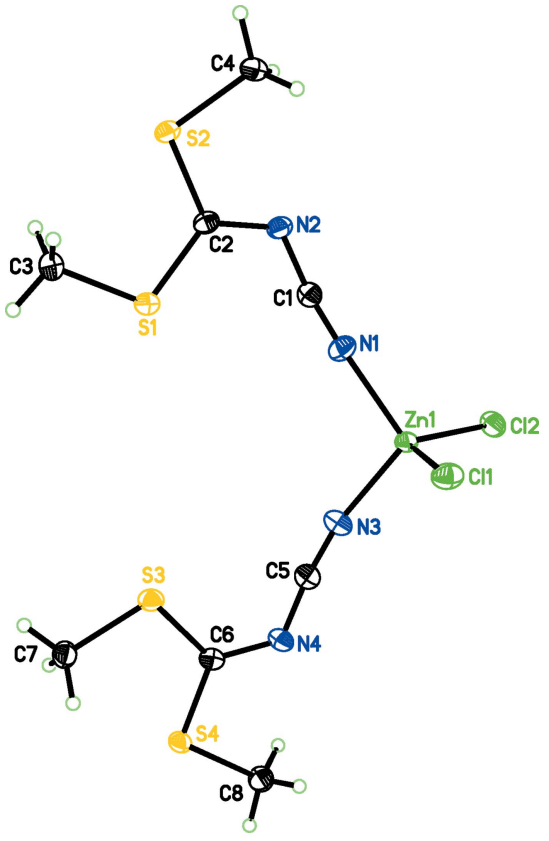


Figure 1
The molecular structure of the title compound. Anisotropic displacement ellipsoids are depicted at the 50% probability level and H atoms as spheres of an arbitrary radius.

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4B···Cl2^{i}	0.98	2.73	3.4486 (18)	131
C3—H3B···Cl1^{ii}	0.98	2.80	3.5868 (19)	137
C7—H7A···Cl2^{iii}	0.98	2.74	3.7165 (18)	176
C7—H7B···Cl1^{ii}	0.98	2.84	3.5976 (18)	134

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

and the cyanide N atoms of two dimethyl *N*-cyanodithioiminocarbonate ligands. The Zn atom has a τ_4 value of 0.94 (Yang *et al.*, 2007), indicating a near ideal tetrahedral geometry (τ_4 = 1 for ideal tetrahedral and 0 for planar environments); $\tau_4 = [360 - (\alpha + \beta)]/141$, where α and β are the two largest tetrahedral angles.

3. Supramolecular features

In the crystal, weak C—H···Cl hydrogen bonds (C3—H3B···Cl1^{ii} and C7—H7B···Cl1^{ii}; Table 1) link the molecules into inversion dimers (Fig. 2). The dimers are connected through a C4—H4B···Cl2^{i} hydrogen bond (Table 1) and an S2···Cl2^{i} short contact [3.3812 (7) Å], giving infinite chains along [$\bar{1}$10]. These chains are then connected through a longer hydrogen bond (C7—H7A···Cl2^{ii}) and an S4···Cl2^{iv} contact

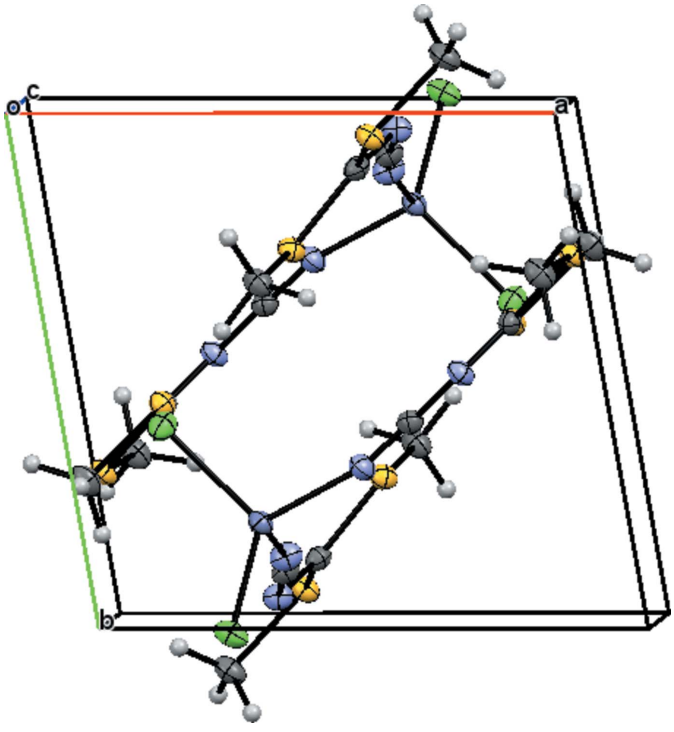


Figure 2
Packing diagram of the title compound, viewed approximately along the *c* axis, showing a pair of molecules. Displacement ellipsoids are as in Fig. 1.

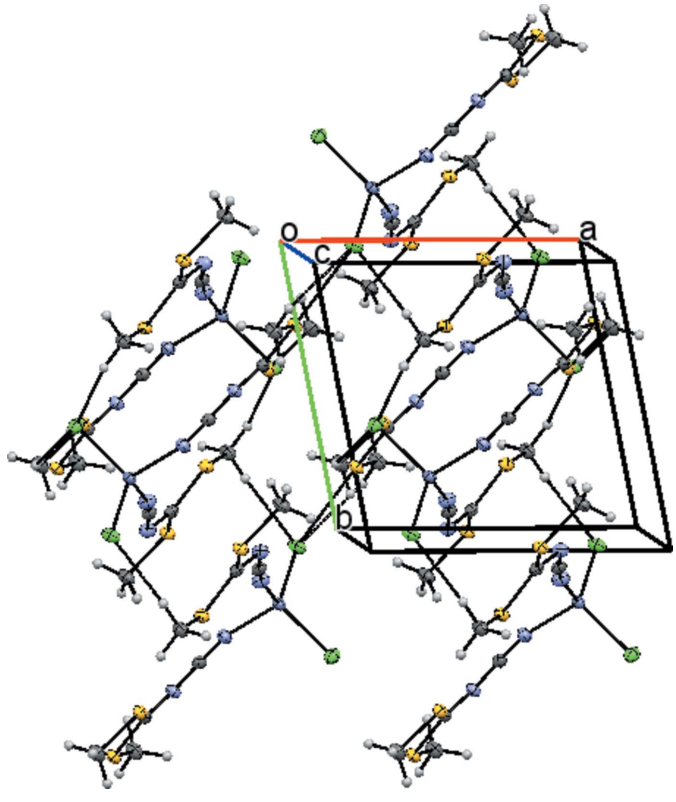


Figure 3
Packing diagram of the title compound viewed approximately along the *c* axis. Displacement ellipsoids are as in Fig. 1.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Zn(C_4H_6N_2S_2)_2Cl_2]$
M_r	428.73
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	120
a, b, c (Å)	8.8574 (5), 8.8833 (6), 11.2391 (7)
α, β, γ (°)	73.0839 (16), 87.4301 (16), 79.9801 (16)
V (Å^3)	833.14 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.29
Crystal size (mm)	0.49 × 0.21 × 0.17
Data collection	
Diffractometer	Bruker Kappa X8 APEXII
Absorption correction	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.520, 0.793
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13605, 4239, 3939
R_{int}	0.019
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.673
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.062, 1.16
No. of reflections	4239
No. of parameters	176
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.71, −0.37

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006).

[3.3765 (7) Å; symmetry code: (iv) $x, y, z + 1$], leading to a layer parallel to the *ab* plane (Fig. 3).

4. Synthesis and crystallization

All chemicals are purchased from Aldrich Company, Germany and used as received. Dimethyl cyanocarbonimidodithioate was mixed in acetonitrile with $ZnCl_2$ in a 1:1 ratio. Colourless block-like single crystals suitable for X-ray diffraction were obtained after a slow solvent evaporation at room temperature (303 K).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was solved by incorporating the coordinates from the isotypic compound $[Co((MeS)_2CNCN)_2Cl_2]$ (Diop *et al.*, 2016). Methyl H atoms were modeled as riding, with C—H = 0.98 Å and with $U_{iso}(H) = 1.5U_{eq}(C)$, and were allowed to rotate to minimize their contribution to the electron density.

Acknowledgements

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Crystal structure of dichloridobis(dimethyl *N*-cyanodithioiminocarbonate)zinc

Mouhamadou Birame Diop, Libasse Diop and Allen G. Oliver

Computing details

Data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2006).

Dichloridobis(dimethyl *N*-cyanodithioiminocarbonate)zinc

Crystal data

$[Zn(C_4H_6N_2S_2)_2Cl_2]$
M_r = 428.73
Triclinic, $P\overline{1}$
a = 8.8574 (5) Å
b = 8.8833 (6) Å
c = 11.2391 (7) Å
α = 73.0839 (16)°
β = 87.4301 (16)°
γ = 79.9801 (16)°
V = 833.14 (9) Å^3
Z = 2
$F(000)$ = 432
D_x = 1.709 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8988 reflections
θ = 2.3–28.6°
μ = 2.29 mm^{-1}
T = 120 K
Block, colourless
0.49 × 0.21 × 0.17 mm

Data collection

Bruker Kappa X8 APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.33 pixels mm^{-1}
combination of ω and φ–scans
Absorption correction: numerical (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.520, T_{max} = 0.793
13605 measured reflections
4239 independent reflections
3939 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.6°, θ_{min} = 1.9°
h = −11→11
k = −9→11
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.062
S = 1.16
4239 reflections
176 parameters
0 restraints
Primary atom site location: isomorphous structure methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.4996P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.31840 (2)	0.80108 (2)	0.23625 (2)	0.01602 (6)
Cl1	0.16956 (5)	0.61543 (5)	0.29276 (4)	0.02386 (9)
Cl2	0.23470 (5)	1.01274 (5)	0.08093 (4)	0.02331 (9)
S1	0.83793 (5)	0.41654 (5)	0.37573 (4)	0.01844 (9)
S2	0.97579 (4)	0.27942 (5)	0.17752 (4)	0.01855 (9)
S3	0.53848 (5)	0.72562 (5)	0.68555 (4)	0.01877 (9)
S4	0.35318 (5)	0.94788 (5)	0.80760 (4)	0.01798 (9)
N1	0.52396 (16)	0.69240 (17)	0.19696 (14)	0.0216 (3)
N2	0.73637 (16)	0.50808 (17)	0.14285 (13)	0.0186 (3)
N3	0.34751 (18)	0.87159 (18)	0.38602 (13)	0.0223 (3)
N4	0.31171 (17)	0.95551 (17)	0.57596 (13)	0.0192 (3)
C1	0.62644 (18)	0.60463 (19)	0.17805 (15)	0.0178 (3)
C2	0.83921 (17)	0.41281 (18)	0.22362 (15)	0.0163 (3)
C3	1.0004 (2)	0.2705 (2)	0.44393 (16)	0.0248 (3)
H3A	0.9886	0.1666	0.4351	0.037*
H3B	1.0075	0.2628	0.5323	0.037*
H3C	1.0940	0.3023	0.4016	0.037*
C4	0.9182 (2)	0.3114 (2)	0.01991 (15)	0.0230 (3)
H4A	0.8123	0.2934	0.0184	0.034*
H4B	0.9859	0.2369	−0.0164	0.034*
H4C	0.9249	0.4213	−0.0285	0.034*
C5	0.33745 (19)	0.90393 (19)	0.47793 (15)	0.0189 (3)
C6	0.39261 (18)	0.88406 (19)	0.67851 (15)	0.0170 (3)
C7	0.6027 (2)	0.6667 (2)	0.84453 (16)	0.0228 (3)
H7A	0.6417	0.7550	0.8617	0.034*
H7B	0.6845	0.5736	0.8586	0.034*
H7C	0.5167	0.6393	0.9000	0.034*
C8	0.1918 (2)	1.1031 (2)	0.75497 (17)	0.0237 (3)
H8A	0.2209	1.1840	0.6817	0.036*
H8B	0.1590	1.1526	0.8213	0.036*
H8C	0.1075	1.0578	0.7330	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01630 (10)	0.01660 (10)	0.01569 (10)	0.00008 (7)	0.00063 (7)	−0.00723 (7)
Cl1	0.02395 (19)	0.0244 (2)	0.0270 (2)	−0.00800 (15)	0.00604 (15)	−0.01198 (16)
Cl2	0.0288 (2)	0.01982 (19)	0.01917 (18)	0.00453 (15)	−0.00438 (15)	−0.00668 (15)
S1	0.01807 (18)	0.02036 (19)	0.01693 (18)	−0.00120 (14)	0.00170 (14)	−0.00684 (14)

S2	0.01730 (18)	0.01884 (19)	0.01817 (18)	0.00245 (14)	0.00138 (14)	−0.00662 (14)
S3	0.02048 (18)	0.01800 (19)	0.01854 (19)	−0.00125 (14)	0.00216 (14)	−0.00781 (14)
S4	0.02055 (18)	0.01868 (19)	0.01489 (17)	0.00057 (14)	−0.00022 (14)	−0.00732 (14)
N1	0.0190 (7)	0.0186 (7)	0.0253 (7)	0.0010 (5)	0.0018 (5)	−0.0062 (6)
N2	0.0176 (6)	0.0185 (6)	0.0183 (6)	0.0011 (5)	0.0019 (5)	−0.0058 (5)
N3	0.0292 (7)	0.0225 (7)	0.0165 (7)	−0.0065 (6)	0.0013 (5)	−0.0069 (5)
N4	0.0243 (7)	0.0190 (7)	0.0150 (6)	−0.0034 (5)	0.0006 (5)	−0.0063 (5)
C1	0.0193 (7)	0.0165 (7)	0.0172 (7)	−0.0032 (6)	−0.0001 (6)	−0.0040 (6)
C2	0.0151 (7)	0.0153 (7)	0.0186 (7)	−0.0032 (5)	0.0031 (5)	−0.0052 (6)
C3	0.0242 (8)	0.0278 (9)	0.0189 (8)	0.0018 (7)	−0.0031 (6)	−0.0044 (7)
C4	0.0245 (8)	0.0267 (9)	0.0174 (8)	0.0016 (7)	0.0007 (6)	−0.0094 (6)
C5	0.0219 (8)	0.0165 (7)	0.0183 (7)	−0.0058 (6)	0.0011 (6)	−0.0036 (6)
C6	0.0193 (7)	0.0162 (7)	0.0168 (7)	−0.0052 (6)	0.0027 (6)	−0.0060 (6)
C7	0.0221 (8)	0.0236 (8)	0.0230 (8)	0.0017 (6)	−0.0043 (6)	−0.0097 (7)
C8	0.0256 (8)	0.0212 (8)	0.0229 (8)	0.0049 (6)	−0.0024 (6)	−0.0090 (7)

Geometric parameters (Å, º)

Zn1—N3	2.0003 (15)	N3—C5	1.146 (2)
Zn1—N1	2.0016 (14)	N4—C5	1.308 (2)
Zn1—Cl2	2.2030 (4)	N4—C6	1.317 (2)
Zn1—Cl1	2.2210 (4)	C3—H3A	0.9800
S1—C2	1.7191 (17)	C3—H3B	0.9800
S1—C3	1.7922 (18)	C3—H3C	0.9800
S2—C2	1.7141 (16)	C4—H4A	0.9800
S2—C4	1.7935 (17)	C4—H4B	0.9800
S3—C6	1.7228 (17)	C4—H4C	0.9800
S3—C7	1.7980 (17)	C7—H7A	0.9800
S4—C6	1.7067 (16)	C7—H7B	0.9800
S4—C8	1.7914 (17)	C7—H7C	0.9800
N1—C1	1.144 (2)	C8—H8A	0.9800
N2—C1	1.309 (2)	C8—H8B	0.9800
N2—C2	1.315 (2)	C8—H8C	0.9800
N3—Zn1—N1	106.61 (6)	H3B—C3—H3C	109.5
N3—Zn1—Cl2	108.82 (5)	S2—C4—H4A	109.5
N1—Zn1—Cl2	110.62 (4)	S2—C4—H4B	109.5
N3—Zn1—Cl1	107.09 (4)	H4A—C4—H4B	109.5
N1—Zn1—Cl1	106.71 (4)	S2—C4—H4C	109.5
Cl2—Zn1—Cl1	116.505 (19)	H4A—C4—H4C	109.5
C2—S1—C3	103.78 (8)	H4B—C4—H4C	109.5
C2—S2—C4	101.50 (8)	N3—C5—N4	172.64 (19)
C6—S3—C7	103.40 (8)	N4—C6—S4	119.94 (13)
C6—S4—C8	101.30 (8)	N4—C6—S3	121.19 (12)
C1—N1—Zn1	166.17 (14)	S4—C6—S3	118.87 (9)
C1—N2—C2	120.32 (15)	S3—C7—H7A	109.5
C5—N3—Zn1	166.98 (14)	S3—C7—H7B	109.5
C5—N4—C6	120.40 (15)	H7A—C7—H7B	109.5

N1—C1—N2	172.98 (18)	S3—C7—H7C	109.5
N2—C2—S2	119.54 (12)	H7A—C7—H7C	109.5
N2—C2—S1	121.40 (12)	H7B—C7—H7C	109.5
S2—C2—S1	119.05 (9)	S4—C8—H8A	109.5
S1—C3—H3A	109.5	S4—C8—H8B	109.5
S1—C3—H3B	109.5	H8A—C8—H8B	109.5
H3A—C3—H3B	109.5	S4—C8—H8C	109.5
S1—C3—H3C	109.5	H8A—C8—H8C	109.5
H3A—C3—H3C	109.5	H8B—C8—H8C	109.5
C1—N2—C2—S2	176.35 (12)	C5—N4—C6—S4	−177.58 (12)
C1—N2—C2—S1	−2.5 (2)	C5—N4—C6—S3	2.2 (2)
C4—S2—C2—N2	−3.57 (15)	C8—S4—C6—N4	2.39 (15)
C4—S2—C2—S1	175.32 (10)	C8—S4—C6—S3	−177.42 (10)
C3—S1—C2—N2	−178.77 (14)	C7—S3—C6—N4	−176.93 (14)
C3—S1—C2—S2	2.36 (12)	C7—S3—C6—S4	2.89 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···Cl2^{i}	0.98	2.73	3.4486 (18)	131
C3—H3*B*···Cl1^{ii}	0.98	2.80	3.5868 (19)	137
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C7—H7*B*···Cl1^{ii}	0.98	2.84	3.5976 (18)	134

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