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1-Cyanomethyl-1,4-diazoniabicyclo-[2.2.2]octane tetrachloridocadmate(II)

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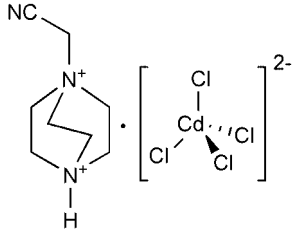
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.026; wR factor = 0.059; data-to-parameter ratio = 21.3.

In the title salt, $(C_8H_{15}N_3)[CdCl_4]$, four Cl atoms coordinate the Cd^{II} atom in a slightly distorted tetrahedral geometry. In the crystal, each $[CdCl_4]^{2-}$ anion is connected to the 1-cyanomethyl-1,4-diazoniabicyclo[2.2.2]octane dications by N—H···Cl hydrogen bonds, forming chains parallel to [001]. C—H···Cl interactions also occur.

Related literature

For the use of 1,4-diazabicyclo[2.2.2]octane (DABCO) and its derivatives, see: Basaviah *et al.* (2003); Zhang, Cheng *et al.* (2009). For ferroelectric properties of DABCO derivatives, see: Zhang, Ye *et al.* (2009, 2010). For related structures, see: Cai (2010); Wei (2010). For the isotypic cobaltate(II) analogue, see: Zhang & Zhu (2012).



Experimental

Crystal data

$(C_8H_{15}N_3)[CdCl_4]$
M_r = 407.43
Monoclinic, $P2_1/c$
a = 8.3747 (17) Å
b = 13.772 (3) Å
c = 12.153 (2) Å
β = 93.89 (3)°
V = 1398.4 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.30 mm^{-1}
T = 298 K
0.36 × 0.32 × 0.28 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.441, T_{max} = 0.525
14246 measured reflections
3200 independent reflections
2899 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.059
S = 1.15
3200 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1···Cl2^{i}	0.79 (3)	2.54 (3)	3.193 (2)	141 (3)
N3—H1···Cl3^{ii}	0.79 (3)	2.76 (3)	3.285 (2)	126 (3)
C1—H1A···Cl3^{iii}	0.97	2.70	3.507 (3)	141 (2)
C3—H3B···Cl4^{iv}	0.97	2.67	3.599 (3)	160 (2)
C4—H4A···Cl1^{i}	0.97	2.81	3.704 (3)	153 (2)
C7—H7A···Cl2^{iv}	0.97	2.61	3.514 (3)	155 (2)
C7—H7B···Cl4^{v}	0.97	2.79	3.489 (3)	129 (2)

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2531).

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supplementary materials

Acta Cryst. (2012). E**68**, m687 [doi:10.1107/S1600536812017801]

1-Cyanomethyl-1,4-diazoniabicyclo[2.2.2]octane tetrachloridocadmate(II)

Yi Zhang and Bo Han Zhu

Comment

1,4-Diazabicyclo[2.2.2]octane (DABCO) is used as a effective organocatalyst for a large number of reactions because of its nucleophilicity (Basaviah *et al.*, 2003) and some of it's derivatives are ferroelectrics (Zhang, Cheng *et al.*, 2009). As part of a systematic investigation of dielectric-ferroelectric materials (Zhang, Ye *et al.*, 2009; 2010), we report the crystal structure of the title compound in this article.

The asymmetric unit of the title compound is composed of cationic $(C_8H_{15}N_3)^{2+}$ and anionic $(CdCl_4)^{2-}$ ions (Fig. 1). The Cd atoms are coordinated by four Cl atoms with very similar distances in the range of 2.2749 (12) to 2.2910 (12) Å. The Cl—Cd—Cl bond angles are between 103.21 (4) and 113.85 (5) ° which shows that the coordination polyhedron can be described as a slightly distorted tetrahedron. The ammonium groups of the organic cations are engaged in bifurcated hydrogen bonds to chlorine atoms of two $(CdCl_4)^{2-}$ anions. These weak N—H···Cl interactions cause the formation of a one-dimensional chain along the [0 0 1] (Fig. 2).

The crystal structures of a few related DABCO derivatives have been reported earlier (Cai, 2010; Wei, 2010).

Experimental

Chloroacetonitrile (0.1 mol, 7.55 g) was added to a CH_3CN (25 ml) solution of 1,4-diaza-bicyclo[2.2.2]octane (DABCO) (0.1 mol, 11.2 g) with stirring for 1 h at room temperature. 1-(Cyanomethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride quickly formed as white solid was filtered, washed with acetonitrile and dried (yield: 80%). $CdCl_2.2.5H_2O$ (0.01 mol, 2.28 g) and 1 g 36% HCl were dissolved in H_2O (20 ml) and 1-(cyanomethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride (0.01 mol, 1.875 g) in H_2O (20 ml) was added. The resulting solution was stirred until a clear solution was obtained. After slow evaporation of the solvent, colourless needle crystals of the title compound suitable for X-ray analysis were obtained in about 60% yield. The title compound has no dielectric disuniform from 80 K to 373 K, (m.p. > 373 K).

Refinement

The C-bound H atoms were positioned geometrically and refined using a riding model with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). The H1 bonded to N3 was located from a difference Fourier map and freely refined.

Computing details

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalClear* (Rigaku, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

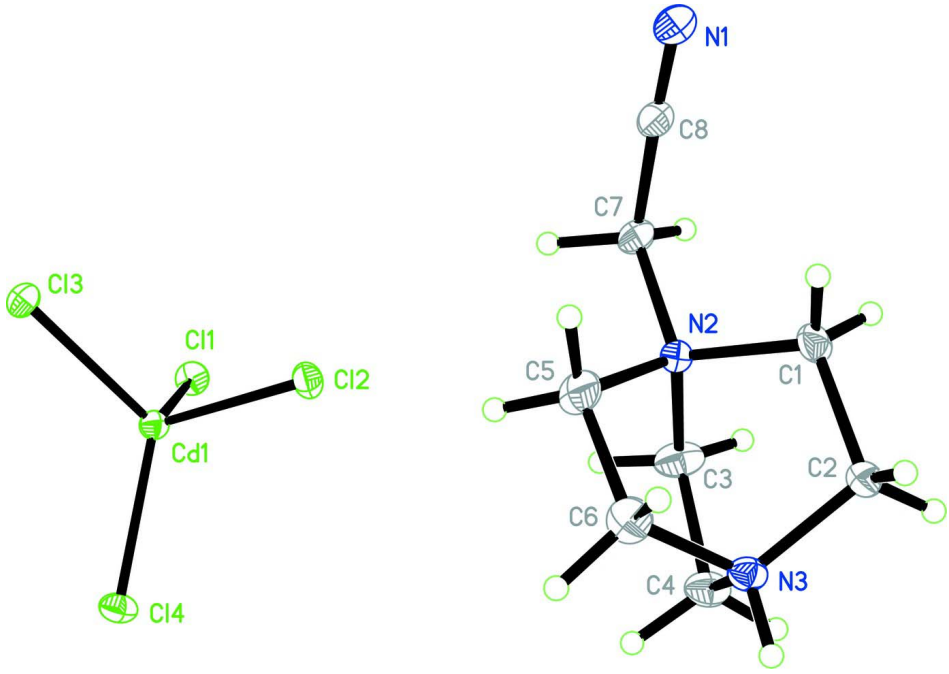

Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as small spheres of arbitrary radius.

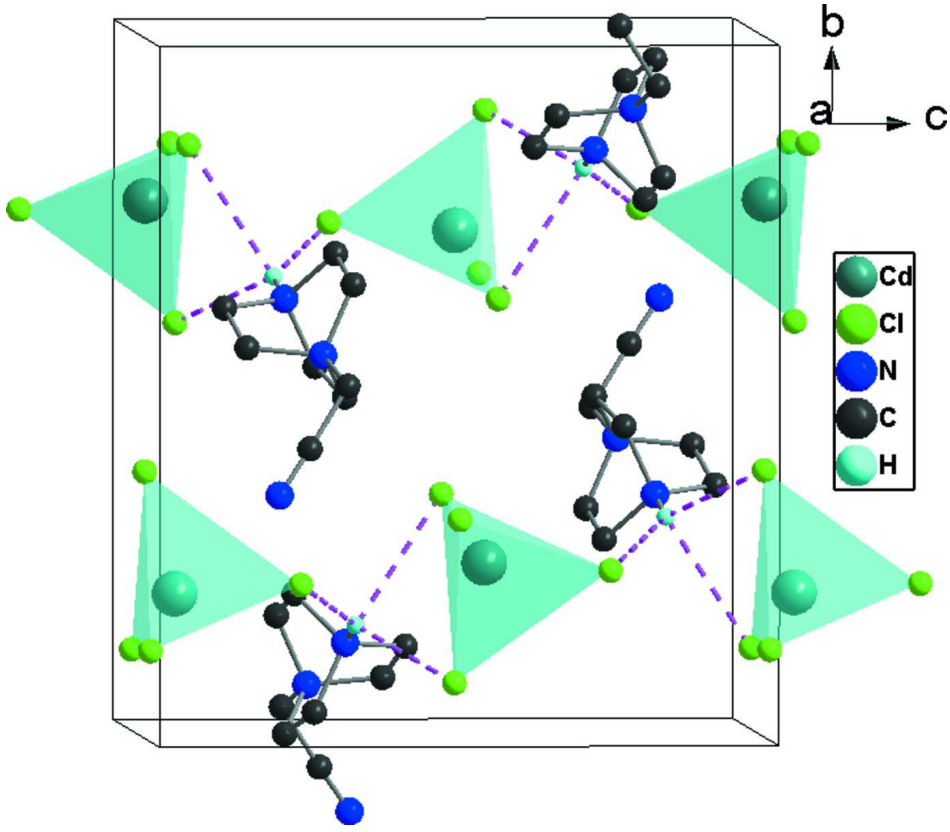

Figure 2

A view of the N—H···Cl hydrogen bonds (dotted lines) in the crystal structure of the title compound. H atoms non-participating in hydrogen-bonding were omitted for clarity.

1-Cyanomethyl-1,4-diazoniabicyclo[2.2.2]octane tetrachloridocadmate(II)

Crystal data

$(C_8H_{15}N_3)[CdCl_4]$
$M_r = 407.43$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.3747$ (17) Å
$b = 13.772$ (3) Å
$c = 12.153$ (2) Å
$\beta = 93.89$ (3)°
$V = 1398.4$ (5) Å^3
$Z = 4$
$F(000) = 800$
$D_x = 1.935$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2622 reflections
$\theta = 3.1$–27.5°
$\mu = 2.30$ mm^{-1}
$T = 298$ K
Needle, colourless
0.36 × 0.32 × 0.28 mm

Data collection

Rigaku SCXmini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.441$, $T_{max} = 0.525$
14246 measured reflections
3200 independent reflections
2899 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$h = -10 \rightarrow 10$
$k = -17 \rightarrow 17$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.059$
$S = 1.15$
3200 reflections
150 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.6019P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0332 (7)

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.

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.77481 (2)	0.228314 (13)	0.006713 (15)	0.02939 (9)
Cl2	0.78074 (8)	0.24012 (5)	0.21119 (5)	0.03509 (16)
Cl3	0.80985 (8)	0.40133 (4)	−0.03853 (5)	0.03183 (15)
Cl4	0.51643 (8)	0.15674 (5)	−0.05148 (5)	0.03630 (16)
Cl1	1.01183 (8)	0.13969 (5)	−0.04509 (6)	0.03678 (16)
N2	0.3731 (2)	0.42550 (13)	0.76461 (15)	0.0207 (4)
C4	0.1866 (3)	0.28852 (19)	0.7311 (2)	0.0314 (6)
H4A	0.1242	0.2852	0.6610	0.038*
H4B	0.1932	0.2238	0.7625	0.038*
N3	0.1084 (2)	0.35561 (15)	0.80727 (17)	0.0259 (4)
C2	0.2107 (3)	0.36440 (19)	0.9119 (2)	0.0286 (5)
H2A	0.2340	0.3005	0.9425	0.034*
H2B	0.1554	0.4016	0.9654	0.034*
C8	0.5761 (3)	0.55142 (19)	0.8006 (2)	0.0318 (6)
C3	0.3525 (3)	0.32615 (19)	0.7140 (2)	0.0350 (6)
H3A	0.4319	0.2822	0.7479	0.042*
H3B	0.3681	0.3295	0.6358	0.042*
C7	0.5335 (3)	0.46373 (17)	0.7366 (2)	0.0279 (5)
H7A	0.6144	0.4143	0.7522	0.033*
H7B	0.5307	0.4787	0.6585	0.033*
C1	0.3652 (3)	0.4152 (2)	0.88691 (19)	0.0305 (5)
H1A	0.3695	0.4788	0.9212	0.037*
H1B	0.4561	0.3778	0.9170	0.037*
N1	0.6122 (3)	0.61640 (17)	0.8522 (2)	0.0438 (6)

C6	0.0823 (3)	0.45326 (19)	0.7556 (2)	0.0359 (6)
H6A	0.0400	0.4978	0.8081	0.043*
H6B	0.0057	0.4484	0.6922	0.043*
C5	0.2410 (3)	0.4904 (2)	0.7198 (3)	0.0401 (7)
H5A	0.2391	0.4918	0.6399	0.048*
H5B	0.2592	0.5560	0.7469	0.048*
H1	0.024 (4)	0.333 (2)	0.817 (3)	0.050 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02778 (12)	0.02888 (12)	0.03141 (13)	−0.00082 (7)	0.00131 (8)	0.00145 (7)
Cl2	0.0308 (3)	0.0461 (4)	0.0282 (3)	0.0020 (3)	0.0009 (3)	0.0045 (3)
Cl3	0.0360 (3)	0.0254 (3)	0.0348 (3)	0.0025 (2)	0.0080 (3)	−0.0005 (2)
Cl4	0.0314 (3)	0.0443 (4)	0.0334 (3)	−0.0076 (3)	0.0032 (3)	−0.0087 (3)
Cl1	0.0341 (3)	0.0352 (3)	0.0414 (4)	0.0051 (3)	0.0048 (3)	−0.0012 (3)
N2	0.0200 (9)	0.0205 (9)	0.0216 (9)	0.0004 (7)	0.0024 (7)	−0.0003 (7)
C4	0.0300 (13)	0.0308 (13)	0.0338 (14)	−0.0037 (10)	0.0046 (11)	−0.0111 (10)
N3	0.0195 (10)	0.0303 (11)	0.0283 (11)	−0.0023 (8)	0.0044 (8)	−0.0023 (8)
C2	0.0292 (13)	0.0334 (13)	0.0234 (12)	−0.0054 (10)	0.0017 (10)	−0.0007 (10)
C8	0.0288 (13)	0.0309 (14)	0.0351 (14)	−0.0056 (10)	−0.0013 (11)	0.0092 (11)
C3	0.0356 (14)	0.0293 (13)	0.0415 (15)	−0.0075 (11)	0.0140 (12)	−0.0176 (11)
C7	0.0250 (12)	0.0286 (12)	0.0306 (13)	−0.0040 (10)	0.0063 (10)	0.0026 (10)
C1	0.0272 (13)	0.0440 (15)	0.0203 (12)	−0.0044 (11)	0.0024 (10)	−0.0012 (10)
N1	0.0557 (16)	0.0299 (12)	0.0442 (14)	−0.0120 (11)	−0.0080 (12)	0.0085 (11)
C6	0.0258 (13)	0.0368 (14)	0.0449 (16)	0.0084 (11)	0.0017 (11)	0.0057 (12)
C5	0.0296 (13)	0.0315 (14)	0.0578 (18)	0.0028 (11)	−0.0060 (12)	0.0187 (13)

Geometric parameters (Å, º)

Cd1—Cl4	2.4385 (8)	C2—H2A	0.9700
Cd1—Cl1	2.4486 (8)	C2—H2B	0.9700
Cd1—Cl3	2.4674 (8)	C8—N1	1.123 (3)
Cd1—Cl2	2.4874 (8)	C8—C7	1.467 (3)
N2—C5	1.496 (3)	C3—H3A	0.9700
N2—C1	1.499 (3)	C3—H3B	0.9700
N2—C7	1.503 (3)	C7—H7A	0.9700
N2—C3	1.505 (3)	C7—H7B	0.9700
C4—N3	1.491 (3)	C1—H1A	0.9700
C4—C3	1.511 (4)	C1—H1B	0.9700
C4—H4A	0.9700	C6—C5	1.515 (4)
C4—H4B	0.9700	C6—H6A	0.9700
N3—C2	1.489 (3)	C6—H6B	0.9700
N3—C6	1.494 (3)	C5—H5A	0.9700
N3—H1	0.79 (3)	C5—H5B	0.9700
C2—C1	1.520 (3)		
Cl4—Cd1—Cl1	116.28 (3)	N2—C3—C4	109.66 (19)
Cl4—Cd1—Cl3	116.26 (3)	N2—C3—H3A	109.7
Cl1—Cd1—Cl3	108.26 (3)	C4—C3—H3A	109.7

Cl4—Cd1—Cl2	105.86 (3)	N2—C3—H3B	109.7
Cl1—Cd1—Cl2	109.14 (3)	C4—C3—H3B	109.7
Cl3—Cd1—Cl2	99.49 (2)	H3A—C3—H3B	108.2
C5—N2—C1	109.6 (2)	C8—C7—N2	110.9 (2)
C5—N2—C7	111.00 (18)	C8—C7—H7A	109.5
C1—N2—C7	110.95 (18)	N2—C7—H7A	109.5
C5—N2—C3	109.5 (2)	C8—C7—H7B	109.5
C1—N2—C3	107.91 (19)	N2—C7—H7B	109.5
C7—N2—C3	107.77 (18)	H7A—C7—H7B	108.0
N3—C4—C3	108.67 (19)	N2—C1—C2	109.70 (19)
N3—C4—H4A	110.0	N2—C1—H1A	109.7
C3—C4—H4A	110.0	C2—C1—H1A	109.7
N3—C4—H4B	110.0	N2—C1—H1B	109.7
C3—C4—H4B	110.0	C2—C1—H1B	109.7
H4A—C4—H4B	108.3	H1A—C1—H1B	108.2
C2—N3—C4	109.2 (2)	N3—C6—C5	108.6 (2)
C2—N3—C6	110.2 (2)	N3—C6—H6A	110.0
C4—N3—C6	110.8 (2)	C5—C6—H6A	110.0
C2—N3—H1	112 (2)	N3—C6—H6B	110.0
C4—N3—H1	107 (2)	C5—C6—H6B	110.0
C6—N3—H1	108 (2)	H6A—C6—H6B	108.4
N3—C2—C1	108.38 (19)	N2—C5—C6	109.6 (2)
N3—C2—H2A	110.0	N2—C5—H5A	109.8
C1—C2—H2A	110.0	C6—C5—H5A	109.8
N3—C2—H2B	110.0	N2—C5—H5B	109.8
C1—C2—H2B	110.0	C6—C5—H5B	109.8
H2A—C2—H2B	108.4	H5A—C5—H5B	108.2
N1—C8—C7	177.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1···Cl2^{i}	0.79 (3)	2.54 (3)	3.193 (2)	141 (3)
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C7—H7*B*···Cl4^{v}	0.97	2.79	3.489 (3)	129 (2)

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