Crystal structure of bis(N,N,N′,N′-tetramethyl-guanidinium) tetrachloridocuprate(II)

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In the structure of the title salt, $(C_5H_{14}N_3)_2[CuCl_4]$, the Cu^{II} atom in the anion lies on a twofold rotation axis. The tetrachloridocuprate(II) anion adopts a flattened tetrahedral coordination environment and interacts electrostatically with the tetramethylguanidinium cation. The crystal packing is additionally consolidated through N—H⋯Cl and C—H⋯Cl hydrogen bonds, resulting in a three-dimensional network structure.

1. Chemical context

The title compound belongs to the series of hybrid organic–inorganic materials of general formula $A_2[MX_4]$ where A is an organic cation, M a divalent transition metal and X a halide. The copper representatives of these families have been extensively studied for their magnetic, dielectric and fluorescent properties in relation to their solid-state structures (Halvorson et al., 1990). Recent studies include examination of polymorphism in relation to electrostatic properties (Awwadi & Haddad, 2012) or thermochroism (Aldrich et al., 2016), sometimes in relation to phase transitions (Kelley et al., 2015).
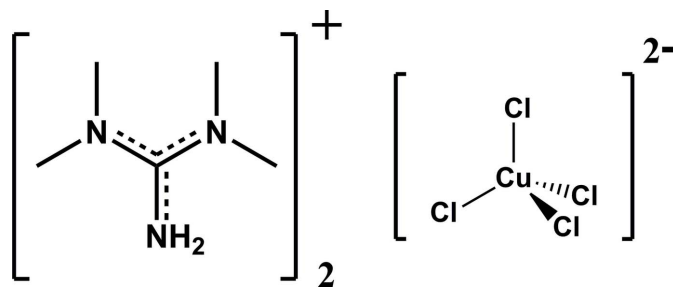
Following our report on the crystal structure of bis-tetramethylguanidinium trichloridocadmate (Ndiaye et al., 2016), we have investigated the interactions between tetramethylguanidine and $CuCl_2 \cdot 2H_2O$ which has yielded the title salt, $(C_5H_{14}N_3)_2[CuCl_4]$, (I).

2. Structural commentary

The asymmetric unit of (I) contains a complete N,N,N′,N′-tetramethylguanidinium cation and half of a $[CuCl_4]^{2-}$ anion held together by an N—H⋯Cl hydrogen bond (Fig. 1). In the anion, the Cu—Cl distances range from 2.2396 (4) Å to 2.2557 (4) Å. They are shorter than those usually found in tetrachloridocuprate(II) anions with a square-planar config-
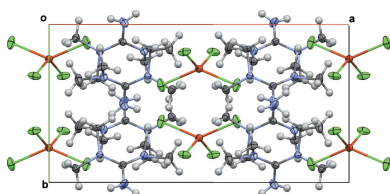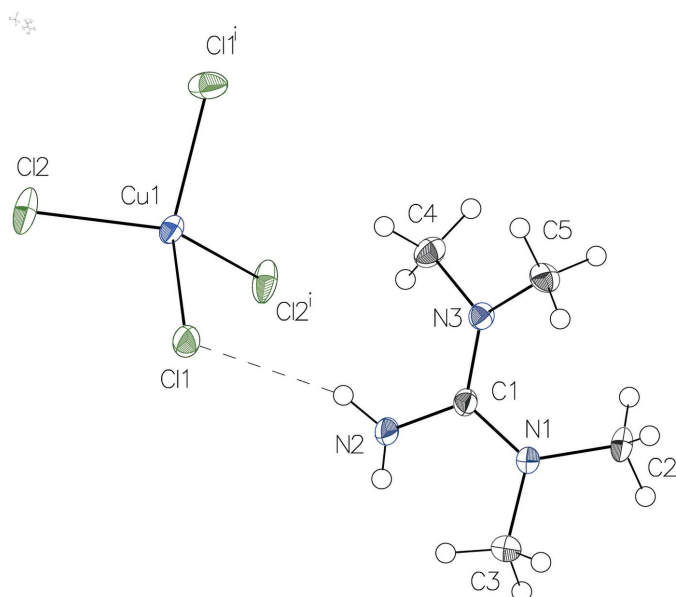
Figure 1
The structures of the molecular entities in (I), drawn with displacement parameters at the 50% probability level. The N—H···Cl hydrogen bond is indicated by a dashed line. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.]

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4B···Cl2^{i}	0.95 (2)	2.77 (2)	3.5902 (19)	145.3 (18)
C2—H2C···Cl1^{ii}	0.98 (3)	2.90 (3)	3.745 (2)	144.5 (18)
C2—H2D···Cl1^{iii}	0.91 (2)	2.91 (2)	3.818 (2)	173.3 (19)
C3—H3B···Cl2^{iv}	0.99 (3)	2.82 (3)	3.793 (2)	168 (2)
C5—H5C···Cl2^{v}	0.93 (3)	2.80 (3)	3.5992 (18)	144.9 (19)
C2—H2E···Cl2^{vi}	0.96 (3)	2.85 (3)	3.6491 (18)	140.5 (19)
N2—H2B···Cl1	0.86 (3)	2.53 (3)	3.3417 (16)	157 (2)

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

uration (Guo *et al.*, 2015). The distortion of the flattened tetrachloridocuprate(II) anion in (I) from the ideal tetrahedral configuration can be asserted by the values of the two *trans* Cl—Cu—Cl angles, 135.62 (3)° and 133.31 (3)°. These two angles can also be used to calculate the τ_4 geometry index developed by Yang *et al.* (2007) for complexes with coordination number four to quantify such a distortion. The τ_4 parameter is defined as $[360 - (\alpha + \beta)] / 141$ where α and β are the two largest Cl—Cu—Cl angles. A τ_4 index value of 1 corresponds to an ideal tetrahedral configuration while a value of 0 is for a perfect square-planar configuration. Here the value obtained (0.65) indicates a 'see-saw' (bisphenoidal) configuration with point group symmetry 2.

In the organic cation, the C—N distances in the central CN$_3$ unit [1.332 (2), 1.335 (2) and 1.342 (2) Å] are consistent with a partial double-bond character and a positive charge delocalization, as usually found in structures involving tetramethylguanidinium cations. The central core of the cation has an almost planar–trigonal geometry, as reflected by the values for the three N—C—N angles close to 120° and the r.m.s deviation from the least-squares plane calculated for atoms C1, N1, N2 and N3 that is only 0.0006 Å. The dimethylammonium groups are twisted by 29.38 (16)° (C2, C3) and 25.08 (16)° (C4, C5) with respect to this plane.

3. Supramolecular features

Anions and cations are connected through electrostatic interactions and *via* classical N—H···Cl hydrogen bonds involving atom Cl1 whereby only one of the H atoms of the amine group is involved; the remaining H atom has no acceptor atom (Fig. 1, Table 1). In addition, each Cl atom of the anion is engaged in three C—H···Cl hydrogen bonds, leading to the formation of a three-dimensional network structure (Fig. 2, Table 1).
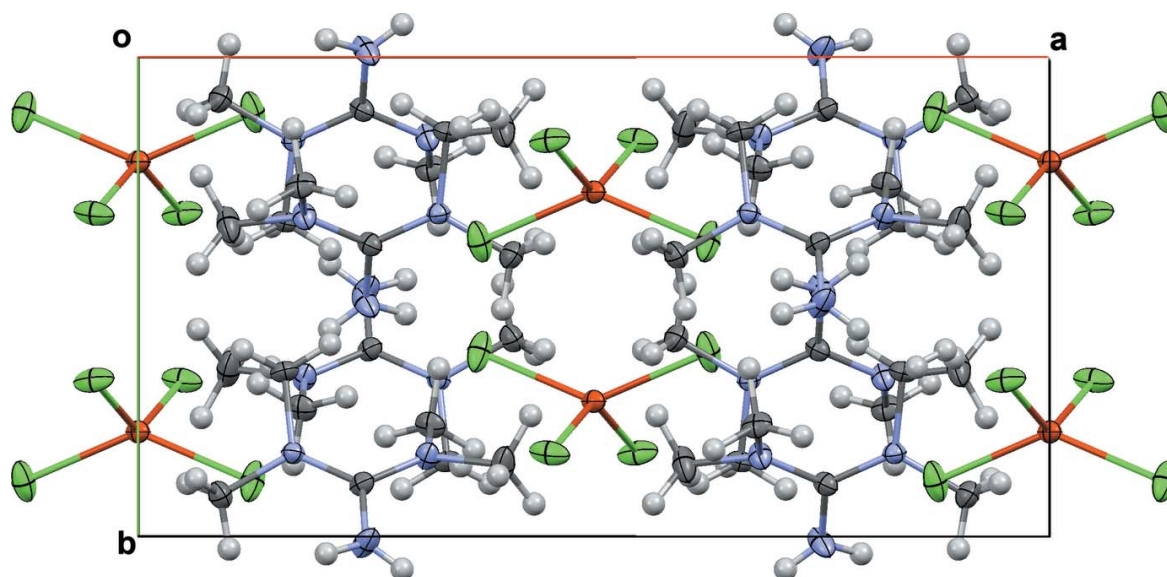

Figure 2
Packing diagram of (I) viewed along [001].

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_5H_{14}N_3)_2[CuCl_4]$
M_r	437.72
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	18.9274 (5), 8.2441 (2), 14.8654 (4)
β (°)	124.165 (1)
V (Å^3)	1919.28 (9)
Z	4
Radiation type	Ga $K\alpha$, $\lambda = 1.34139$ Å
μ (mm^{-1})	9.51
Crystal size (mm)	$0.16 \times 0.10 \times 0.06$
Data collection	
Diffractometer	Bruker Venture Metaljet
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.449, 0.752
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14222, 2208, 2178
R_{int}	0.036
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.071, 1.11
No. of reflections	2208
No. of parameters	152
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.84, −0.35

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

4. Database survey

A search in the Cambridge Structural Database (Version 5.37 with two updates; Groom *et al.*, 2016) for isolated tetra-chloridocuprate(II) anions without disorder returned 342 hits for a total of 389 fragments. The configurations of these fragments were analysed using the τ_4 index as described above. Around 60 of these (15%) have a τ_4 index value less than 0.1, including 29 that have a τ_4 index of 0 (ideal square-planar configuration). Only four were found to have a configuration close to the ideal tetrahedral one with a τ_4 index value larger than 0.9. A large number of fragments (72%) has a geometry index τ_4 value in the 0.6–0.8 range and feature a bisphenoidal configuration as found for (I). An analysis with the modified version of the τ_4 index [τ_4', as defined by Okuniewski *et al.* (2015)] gives a similar distribution with only minor variation.

The title compound is isostructural with bis(*N*,*N*,*N'*,*N'*-tetramethylguanidinium) tetrabromidonickelate(II) (Jones & Thonnessen, 2006) and shows similarities in terms of the space-group and cell parameters with tetramethylguanidinium bisulfite (Heldebrant *et al.*, 2009).

5. Synthesis and crystallization

Yellowish-green crystals were obtained by mixing in stoichiometric amounts tetramethylguanidine with $CuCl_2 \cdot 2H_2O$ in ethanol.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located from a Fourier difference map and were refined freely.

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supporting information

Crystal structure of bis(*N*,*N*,*N*′,*N*′-tetramethylguanidinium) tetrachloridocuprate(II)

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

Bis(*N*,*N*,*N*′,*N*′-tetramethylguanidinium) tetrachloridocuprate(II)

Crystal data

$(C_5H_{14}N_3)_2[CuCl_4]$	$F(000) = 908$
$M_r = 437.72$	$D_x = 1.515$ Mg m^{-3}
Monoclinic, $C2/c$	Ga $K\alpha$ radiation, $\lambda = 1.34139$ Å
$a = 18.9274$ (5) Å	Cell parameters from 9968 reflections
$b = 8.2441$ (2) Å	$\theta = 4.9$–60.7°
$c = 14.8654$ (4) Å	$\mu = 9.51$ mm^{-1}
$\beta = 124.165$ (1)°	$T = 100$ K
$V = 1919.28$ (9) Å^3	Block, clear yellowish green
$Z = 4$	$0.16 \times 0.10 \times 0.06$ mm

Data collection

Bruker Venture Metaljet diffractometer	$T_{min} = 0.449$, $T_{max} = 0.752$
Radiation source: Metal Jet, Gallium Liquid Metal Jet Source	14222 measured reflections
	2208 independent reflections
Helios MX Mirror Optics monochromator	2178 reflections with $I > 2\sigma(I)$
Detector resolution: 10.24 pixels mm^{-1}	$R_{int} = 0.036$
ω and φ scans	$\theta_{max} = 60.7°$, $\theta_{min} = 4.9°$
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)	$h = -24 \rightarrow 24$
	$k = -10 \rightarrow 10$
	$l = -16 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.028$	All H-atom parameters refined
$wR(F^2) = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 2.7253P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	
2208 reflections	$(\Delta/\sigma)_{max} = 0.001$
152 parameters	$\Delta\rho_{max} = 0.84$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

Experimental. X-ray crystallographic data for I were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker Venture diffractometer equipped with a Photon 100 CMOS Detector, a Helios MX optics and a Kappa goniometer. The crystal-to-detector distance was 4.0 cm, and the data collection was carried out in 1024 x 1024 pixel mode.

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.18244 (9)	0.33219 (19)	0.30111 (11)	0.0202 (3)
N2	0.24981 (11)	0.5129 (2)	0.44495 (13)	0.0277 (4)
N3	0.32977 (9)	0.32615 (17)	0.42260 (11)	0.0164 (3)
C1	0.25428 (10)	0.3903 (2)	0.38962 (13)	0.0173 (3)
C2	0.17917 (12)	0.2676 (2)	0.20725 (14)	0.0215 (3)
C3	0.09950 (12)	0.3500 (3)	0.28512 (17)	0.0314 (4)
C4	0.40978 (11)	0.4132 (2)	0.49381 (15)	0.0235 (4)
C5	0.33922 (12)	0.1564 (2)	0.40153 (15)	0.0208 (3)
Cu1	0.5000	0.71829 (4)	0.7500	0.01698 (11)
Cl1	0.37443 (3)	0.61496 (7)	0.70754 (4)	0.03106 (13)
Cl2	0.54835 (3)	0.82595 (5)	0.91317 (3)	0.02989 (13)
H4A	0.4363 (15)	0.380 (3)	0.569 (2)	0.030 (6)*
H5A	0.2894 (16)	0.099 (3)	0.3780 (19)	0.029 (6)*
H4B	0.4000 (14)	0.526 (3)	0.4851 (18)	0.024 (5)*
H2C	0.1702 (16)	0.150 (3)	0.2047 (19)	0.030 (6)*
H2D	0.2285 (15)	0.291 (3)	0.2132 (18)	0.022 (5)*
H3A	0.0693 (18)	0.248 (4)	0.260 (2)	0.040 (7)*
H2A	0.2102 (18)	0.568 (4)	0.418 (2)	0.037 (7)*
H3B	0.0655 (19)	0.432 (4)	0.228 (2)	0.050 (8)*
H5B	0.3539 (15)	0.147 (3)	0.349 (2)	0.028 (6)*
H5C	0.3857 (16)	0.111 (3)	0.465 (2)	0.028 (6)*
H2E	0.1316 (16)	0.319 (3)	0.143 (2)	0.028 (6)*
H4C	0.4454 (16)	0.389 (3)	0.468 (2)	0.033 (6)*
H2B	0.2934 (17)	0.536 (3)	0.509 (2)	0.035 (6)*
H3C	0.1050 (17)	0.373 (3)	0.352 (2)	0.040 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0176 (6)	0.0242 (7)	0.0155 (6)	0.0023 (6)	0.0072 (5)	−0.0054 (6)
N2	0.0225 (7)	0.0289 (8)	0.0186 (7)	0.0092 (7)	0.0036 (6)	−0.0097 (6)
N3	0.0174 (6)	0.0135 (6)	0.0163 (6)	−0.0003 (5)	0.0083 (5)	−0.0008 (5)
C1	0.0196 (7)	0.0167 (7)	0.0130 (7)	0.0028 (6)	0.0075 (6)	−0.0001 (6)
C2	0.0273 (9)	0.0215 (9)	0.0134 (8)	−0.0026 (7)	0.0102 (7)	−0.0044 (6)
C3	0.0182 (8)	0.0432 (12)	0.0264 (9)	0.0061 (8)	0.0086 (7)	−0.0100 (9)
C4	0.0194 (8)	0.0228 (9)	0.0223 (8)	−0.0040 (7)	0.0079 (7)	−0.0029 (7)

C5	0.0234 (8)	0.0132 (7)	0.0253 (9)	0.0028 (7)	0.0135 (7)	0.0000 (7)
Cu1	0.01872 (18)	0.01483 (18)	0.01209 (17)	0.000	0.00542 (14)	0.000
Cl1	0.0201 (2)	0.0510 (3)	0.0243 (2)	−0.00970 (18)	0.01383 (17)	−0.01532 (19)
Cl2	0.0501 (3)	0.0180 (2)	0.01273 (19)	−0.00519 (18)	0.01222 (18)	−0.00224 (14)

Geometric parameters (Å, °)

N1—C1	1.342 (2)	C3—H3B	0.99 (3)
N1—C2	1.462 (2)	C3—H3C	0.96 (3)
N1—C3	1.457 (2)	C4—H4A	0.97 (3)
N2—C1	1.335 (2)	C4—H4B	0.95 (2)
N2—H2A	0.77 (3)	C4—H4C	0.97 (3)
N2—H2B	0.86 (3)	C5—H5A	0.93 (3)
N3—C1	1.332 (2)	C5—H5B	0.96 (2)
N3—C4	1.459 (2)	C5—H5C	0.93 (3)
N3—C5	1.467 (2)	Cu1—Cl1^i	2.2557 (4)
C2—H2C	0.98 (3)	Cu1—Cl1	2.2557 (4)
C2—H2D	0.91 (2)	Cu1—Cl2^i	2.2396 (4)
C2—H2E	0.96 (3)	Cu1—Cl2	2.2396 (4)
C3—H3A	0.96 (3)		
C1—N1—C2	122.85 (14)	H3A—C3—H3B	108 (2)
C1—N1—C3	121.97 (14)	H3A—C3—H3C	105 (2)
C3—N1—C2	114.63 (14)	H3B—C3—H3C	113 (2)
C1—N2—H2A	120 (2)	N3—C4—H4A	110.4 (14)
C1—N2—H2B	119.9 (17)	N3—C4—H4B	110.0 (14)
H2A—N2—H2B	120 (3)	N3—C4—H4C	106.3 (15)
C1—N3—C4	122.24 (14)	H4A—C4—H4B	112 (2)
C1—N3—C5	122.31 (14)	H4A—C4—H4C	112 (2)
C4—N3—C5	115.01 (14)	H4B—C4—H4C	106 (2)
N2—C1—N1	119.64 (15)	N3—C5—H5A	110.2 (15)
N3—C1—N1	120.38 (15)	N3—C5—H5B	111.8 (15)
N3—C1—N2	119.98 (15)	N3—C5—H5C	109.2 (15)
N1—C2—H2C	108.1 (14)	H5A—C5—H5B	110 (2)
N1—C2—H2D	109.8 (14)	H5A—C5—H5C	111 (2)
N1—C2—H2E	107.2 (15)	H5B—C5—H5C	104 (2)
H2C—C2—H2D	111 (2)	Cl1—Cu1—Cl1^i	135.62 (3)
H2C—C2—H2E	110 (2)	Cl2—Cu1—Cl1	100.265 (17)
H2D—C2—H2E	110 (2)	Cl2^i—Cu1—Cl1	96.958 (19)
N1—C3—H3A	109.1 (16)	Cl2—Cu1—Cl1^i	96.959 (19)
N1—C3—H3B	109.1 (17)	Cl2^i—Cu1—Cl1^i	100.264 (17)
N1—C3—H3C	111.8 (16)	Cl2—Cu1—Cl2^i	133.31 (3)
C2—N1—C1—N2	146.94 (18)	C4—N3—C1—N1	159.80 (16)
C2—N1—C1—N3	−33.3 (3)	C4—N3—C1—N2	−20.4 (2)

| C3—N1—C1—N2 | −24.1 (3) | C5—N3—C1—N1 | −28.2 (2) |
| C3—N1—C1—N3 | 155.67 (18) | C5—N3—C1—N2 | 151.61 (17) |

Symmetry code: (i) −x+1, y, −z+3/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4B···Cl2[i]	0.95 (2)	2.77 (2)	3.5902 (19)	145.3 (18)
C2—H2C···Cl1[ii]	0.98 (3)	2.90 (3)	3.745 (2)	144.5 (18)
C2—H2D···Cl1[iii]	0.91 (2)	2.91 (2)	3.818 (2)	173.3 (19)
C3—H3B···Cl2[iv]	0.99 (3)	2.82 (3)	3.793 (2)	168 (2)
C5—H5C···Cl2[v]	0.93 (3)	2.80 (3)	3.5992 (18)	144.9 (19)
C2—H2E···Cl2[vi]	0.96 (3)	2.85 (3)	3.6491 (18)	140.5 (19)
N2—H2B···Cl1	0.86 (3)	2.53 (3)	3.3417 (16)	157 (2)

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