Crystal structure of the monoclinic phase (phase IV) of bis(tetramethylammonium) tetrachloridocuprate(II)

Gorgui Awa Seck,[a] Libasse Diop[a]* and Allen G. Oliver[b]

[a]Laboratoire de Chimie Minérale et Analytique, Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal, and [b]Department of Chemistry and Biochemistry, University of Notre Dame, IN 46557-5670, USA. *Correspondence e-mail: dlibasse@gmail.com

The crystal structure of the low-temperature monoclinic phase of the title compound, $[(CH_3)_4N]_2[CuCl_4]$, was determined at 120 K. The structure of the room-temperature phase has been determined in the orthorhombic space group *Pmcm* [Morosin & Lingafelter (1961). *J. Phys. Chem.* 50–51; Clay *et al.* (1975). *Acta Cryst.* B**31** 289–290]. The asymmetric unit consists of one discrete tetrachloridocuprate anion with a distorted tetrahedral geometry and two tetramethylammonium cations. In the crystal, the cations and the anions are linked *via* weak C—H···Cl hydrogen bonds.

1. Chemical context

The title compound undergoes successive phase transitions at 297, 291 and 263 K (Sugiyama *et al.*, 1980). The room temperature phase (phase I) crystallizes in the orthorhombic space group *Pmcm* with Z = 4 (Morosin & Lingafelter, 1961; Clay *et al.*, 1975). Three low-temperature phases, named phases II, III and IV in the order of decreasing temperature, show incommensurate, ferroelastic commensurate monoclinic and monoclinic structures, respectively (Sugiyama *et al.*, 1980; Gesi & Iizumi, 1980). We allowed $[(CH_3)_4N]Cl$, $CuCl_2$ and thioacetamide to react in ethanol. The expected mixed ligand complex was not crystallized but instead the title compound was obtained accidentally. The crystal structure of phase IV of the title compound was determined at 120 K and is reported herein.
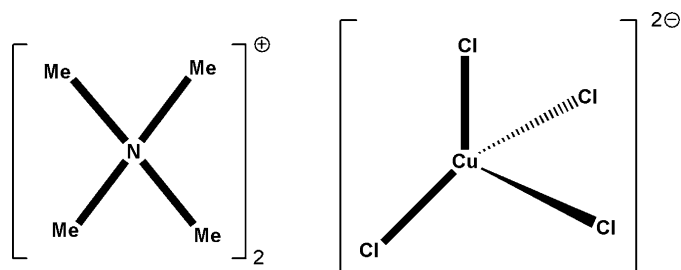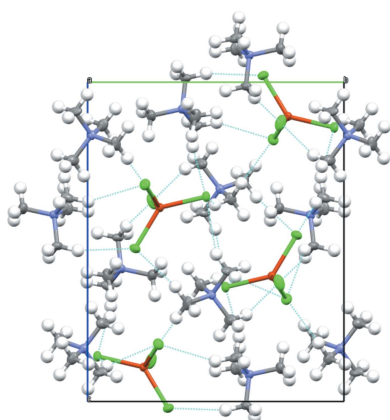
2. Structural commentary

The asymmetric unit of the title compound consists of a discrete $[CuCl_4]^{2-}$ anion and two crystallographically tetra-methylammonium cations (Fig. 1). In the anion, the four Cl atoms are inequivalent with Cu—Cl distances ranging from 2.2313 (15) to 2.2538 (16) Å. The Cl—Cu—Cl angles vary from 98.44 (7) to 133.69 (7)°, indicating a distorted tetrahedral
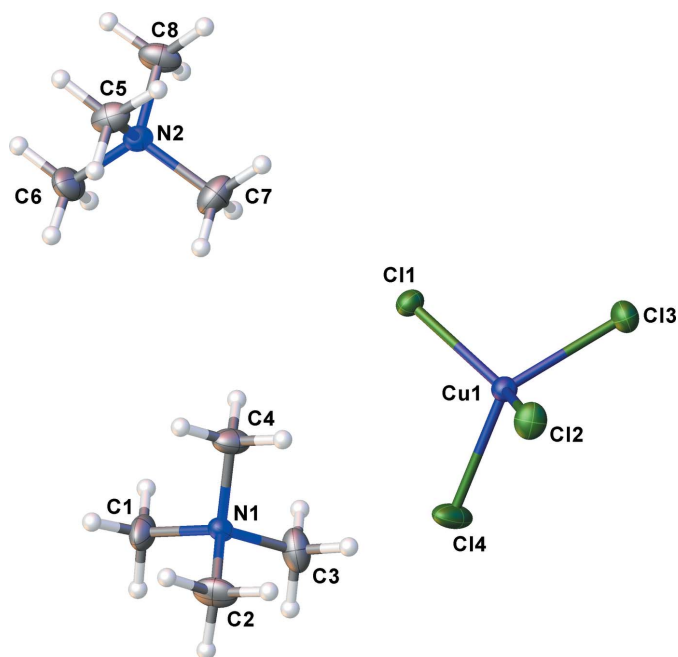
Figure 1
The asymmetric unit of the title compound showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of an arbitrary radius.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$C\cdots$Cl2^{i}	0.98	2.69	3.585 (7)	153
C2—H2$A\cdots$Cl1^{ii}	0.98	2.79	3.675 (7)	151
C2—H2$A\cdots$Cl3^{ii}	0.98	2.80	3.555 (7)	134
C2—H2$B\cdots$Cl1^{i}	0.98	2.79	3.674 (7)	150
C3—H3$B\cdots$Cl4	0.98	2.74	3.670 (7)	159
C4—H4$A\cdots$Cl3^{iii}	0.98	2.59	3.555 (7)	166
C5—H5$A\cdots$Cl2^{iv}	0.98	2.68	3.635 (7)	165
C5—H5$B\cdots$Cl3^{v}	0.98	2.81	3.587 (6)	137
C5—H5$C\cdots$Cl4^{i}	0.98	2.63	3.610 (6)	173
C8—H8$B\cdots$Cl1^{iii}	0.98	2.76	3.650 (6)	151
C8—H8$C\cdots$Cl2^{v}	0.98	2.82	3.763 (7)	162

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

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were included in idealized geometries and allowed to rotate to minimize their electron-density contribution with C—H = 0.98 Å and U_{iso}(H) = $1.5U_{eq}$(C). The crystal used was found to be twinned through a 180° rotation about the reciprocal a axis with a twin component ratio of 0.76:0.24 (matrix: [1.000 −0.003 0.004 0.001 −1.000 −0.003 −0.093 0.005 −1.000]) . The diffraction data were integrated routinely applying this matrix and were scaled for absorption effects using *TWINABS* (Krause *et al.*, 2015). In the final model, incorporation of the twinned data did not

geometry around the Cu^{II} atom. Using Houser's τ_4 metric [$\tau_4 = 360 - (\alpha + \beta)/141$], where α and β are the largest angles about the metal atom (Yang *et al.*, 2007), we obtain a value of 0.658 for phase IV and 0.792 for the orthorhombic phase I. This indicates a greater deviation from an ideal tetrahedron in phase IV compared with phase I, tending towards a 'see-saw' geometry.

3. Supramolecular features

In the crystal, the cations and the anions are linked *via* weak C—H$\cdots$Cl hydrogen bonds (Table 1 and Fig. 2), forming a three-dimensional network.

4. Database survey

A substructure search for compounds that incorporate a tetramethylammonium ion and a copper tetrachloride species reveals thirteen structures (CSD November 2016; Groom *et al.*, 2016). Of these, three are structures of (Me$_4$N)$_2$[CuCl$_4$] with a discrete [CuCl$_4$]$^{2-}$ anion (Morosin & Lingafelter, 1961; Clay *et al.*, 1975; Hlel *et al.*, 2008).

5. Synthesis and crystallization

On mixing [(CH$_3$)$_4$N]Cl (0.465 g, 4.2 mmol) in ethanol (10 ml) with CuCl$_2$·2H$_2$O (0.365 g, 2.1 mmol) in ethanol (10 ml) and thioacetamide (0.160 g, 2.1 mmol) in ethanol (10 ml), a clear solution is obtained. Slow evaporation at room temperature (301 K) yielded pale-green crystals of [(CH$_3$)$_4$N]$_2$[CuCl$_4$] suitable for X-ray determination.
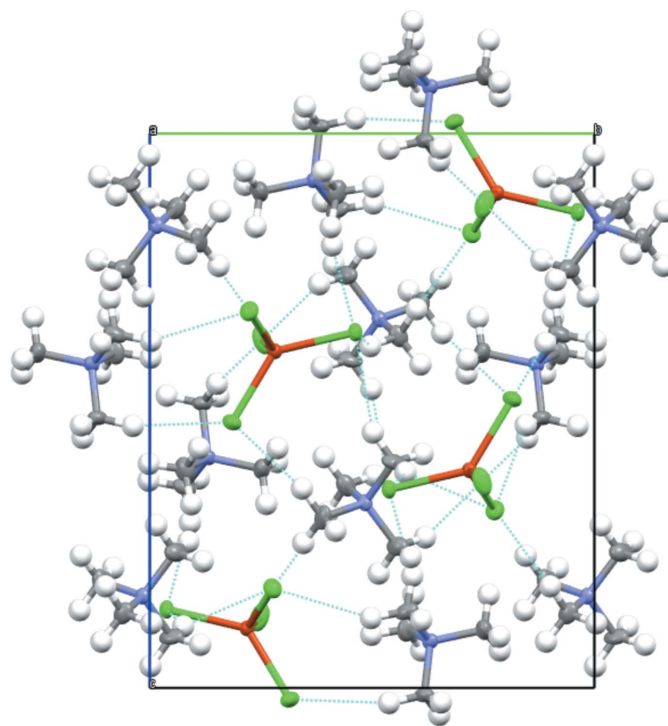

Figure 2
A packing diagram of the title compound, viewed along the *a* axis, showing the C—H$\cdots$Cl hydrogen bonds (blue dashed lines).

research communications

significantly alter the model, thus the final model was refined using the majority component data.

References

Bruker (2015). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Clay, R., Murray-Rust, J. & Murray-Rust, P. (1975). *Acta Cryst.* B**31**, 289–290.

Gesi, K. & Iizumi, M. (1980). *J. Phys. Soc. Jpn*, **48**, 1775–1776.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hlel, F., Ben Rhaeim, A. & Guidara, K. (2008). *Zh. Neorg. Khim.* **53**, 785–793.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Morosin, B. & Lingafelter, E. C. (1961). *J. Phys. Chem.* **65**, 50–51.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Sugiyama, J., Wada, M., Sawada, A. & Ishibashi, Y. (1980). *J. Phys. Soc. Jpn*, **49**, 1405–1412.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Yang, L., Powell, D. R. & Houser, R. P. (2007). *Dalton Trans.* pp. 955–964.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_4H_{12}N)_2[CuCl_4]$
M_r	353.63
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, b, c (Å)	8.9901 (5), 12.0059 (7), 14.9570 (9)
β (°)	91.719 (3)
V (Å^3)	1613.65 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.99
Crystal size (mm)	$0.15 \times 0.12 \times 0.11$
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (*TWINABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.659, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7842, 4019, 2862
R_{int}	0.057
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.066, 0.141, 1.12
No. of reflections	4019
No. of parameters	144
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.16, −1.03

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *XP* in *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

Crystal structure of the monoclinic phase (phase IV) of bis(tetramethyl-ammonium) tetrachloridocuprate(II)

Gorgui Awa Seck, Libasse Diop and Allen G. Oliver

Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXT* (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: *publCIF* (Westrip, 2010).

Bis(tetramethylammonium) tetrachloridocuprate(II)

Crystal data

$(C_4H_{12}N)_2[CuCl_4]$	$F(000) = 732$
$M_r = 353.63$	$D_x = 1.456$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.9901$ (5) Å	Cell parameters from 6598 reflections
$b = 12.0059$ (7) Å	$\theta = 2.6$–24.7°
$c = 14.9570$ (9) Å	$\mu = 1.99$ mm^{-1}
$\beta = 91.719$ (3)°	$T = 120$ K
$V = 1613.65$ (16) Å^3	Block, pale green
$Z = 4$	$0.15 \times 0.12 \times 0.11$ mm

Data collection

Bruker APEXII diffractometer	7842 measured reflections
Radiation source: fine-focus sealed tube	4019 independent reflections
Graphite monochromator	2862 reflections with $I > 2\sigma(I)$
Detector resolution: 8.33 pixels mm^{-1}	$R_{int} = 0.057$
combination of ω and φ–scans	$\theta_{max} = 28.4°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (*TWINABS*; Krause *et al.*, 2015)	$h = -12 \rightarrow 12$
	$k = -16 \rightarrow 16$
$T_{min} = 0.659$, $T_{max} = 0.746$	$l = 0 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: real-space vector search
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.066$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.141$	
$S = 1.12$	Hydrogen site location: inferred from neighbouring sites
4019 reflections	
144 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + 15.8242P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -1.03$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.77037 (7)	0.71890 (6)	0.60734 (5)	0.01762 (17)
Cl1	0.78370 (15)	0.53786 (11)	0.64164 (10)	0.0211 (3)
Cl2	0.79189 (17)	0.81507 (13)	0.47896 (10)	0.0275 (3)
Cl3	0.97801 (15)	0.77628 (13)	0.67958 (10)	0.0267 (3)
Cl4	0.52836 (16)	0.74708 (14)	0.62755 (13)	0.0363 (4)
N1	0.2548 (5)	0.4839 (4)	0.6659 (3)	0.0183 (10)
C1	0.1601 (7)	0.3893 (5)	0.6925 (5)	0.0322 (15)
H1A	0.0671	0.4177	0.7162	0.048*
H1B	0.2128	0.3452	0.7386	0.048*
H1C	0.1378	0.3422	0.6403	0.048*
C2	0.1815 (7)	0.5491 (6)	0.5923 (4)	0.0328 (15)
H2A	0.0840	0.5750	0.6113	0.049*
H2B	0.1685	0.5017	0.5392	0.049*
H2C	0.2436	0.6133	0.5779	0.049*
C3	0.2801 (7)	0.5574 (6)	0.7446 (5)	0.0344 (16)
H3A	0.1846	0.5868	0.7639	0.052*
H3B	0.3451	0.6192	0.7284	0.052*
H3C	0.3273	0.5146	0.7935	0.052*
C4	0.4008 (6)	0.4411 (6)	0.6347 (5)	0.0296 (14)
H4A	0.4516	0.4002	0.6834	0.044*
H4B	0.4629	0.5038	0.6167	0.044*
H4C	0.3836	0.3912	0.5836	0.044*
N2	0.7505 (5)	0.1309 (4)	0.5840 (3)	0.0198 (10)
C5	0.7809 (7)	0.1175 (6)	0.4871 (4)	0.0279 (14)
H5A	0.7882	0.0381	0.4727	0.042*
H5B	0.8748	0.1545	0.4738	0.042*
H5C	0.6998	0.1511	0.4512	0.042*
C6	0.6058 (7)	0.0788 (6)	0.6059 (5)	0.0334 (16)
H6A	0.6112	−0.0018	0.5957	0.050*
H6B	0.5264	0.1106	0.5675	0.050*
H6C	0.5846	0.0931	0.6687	0.050*
C7	0.7444 (8)	0.2520 (5)	0.6048 (5)	0.0347 (16)
H7A	0.7225	0.2622	0.6681	0.052*
H7B	0.6661	0.2872	0.5676	0.052*
H7C	0.8405	0.2863	0.5925	0.052*
C8	0.8722 (7)	0.0776 (6)	0.6381 (4)	0.0304 (15)

H8A	0.8733	−0.0026	0.6260	0.046*
H8B	0.8558	0.0901	0.7018	0.046*
H8C	0.9678	0.1102	0.6222	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0169 (3)	0.0172 (3)	0.0188 (3)	0.0000 (3)	0.0018 (2)	0.0003 (3)
Cl1	0.0216 (7)	0.0157 (6)	0.0261 (7)	0.0009 (5)	0.0031 (5)	0.0006 (5)
Cl2	0.0355 (8)	0.0277 (8)	0.0195 (7)	−0.0040 (6)	0.0024 (6)	0.0043 (6)
Cl3	0.0227 (7)	0.0268 (8)	0.0304 (8)	−0.0034 (6)	−0.0019 (6)	−0.0028 (6)
Cl4	0.0169 (7)	0.0303 (8)	0.0621 (12)	0.0049 (6)	0.0097 (7)	0.0129 (8)
N1	0.014 (2)	0.018 (2)	0.022 (3)	0.0001 (18)	−0.0003 (18)	0.0018 (19)
C1	0.028 (3)	0.022 (3)	0.047 (4)	−0.010 (3)	0.012 (3)	−0.005 (3)
C2	0.030 (3)	0.048 (4)	0.020 (3)	0.013 (3)	−0.004 (3)	0.007 (3)
C3	0.038 (4)	0.037 (4)	0.028 (4)	−0.016 (3)	−0.001 (3)	−0.001 (3)
C4	0.020 (3)	0.030 (4)	0.038 (4)	0.006 (3)	0.008 (3)	0.007 (3)
N2	0.020 (2)	0.020 (2)	0.019 (3)	0.0022 (19)	0.0043 (19)	0.0018 (19)
C5	0.036 (4)	0.031 (3)	0.016 (3)	0.009 (3)	0.002 (3)	0.001 (3)
C6	0.021 (3)	0.031 (4)	0.048 (4)	−0.006 (3)	0.007 (3)	0.005 (3)
C7	0.051 (4)	0.022 (3)	0.032 (4)	0.001 (3)	0.009 (3)	−0.002 (3)
C8	0.025 (3)	0.043 (4)	0.023 (3)	0.009 (3)	0.001 (2)	0.010 (3)

Geometric parameters (Å, º)

Cu1—Cl4	2.2313 (15)	C4—H4B	0.9800
Cu1—Cl1	2.2357 (15)	C4—H4C	0.9800
Cu1—Cl3	2.2374 (15)	N2—C8	1.486 (7)
Cu1—Cl2	2.2538 (16)	N2—C7	1.488 (8)
N1—C1	1.481 (7)	N2—C6	1.488 (7)
N1—C3	1.483 (8)	N2—C5	1.491 (7)
N1—C2	1.488 (7)	C5—H5A	0.9800
N1—C4	1.498 (7)	C5—H5B	0.9800
C1—H1A	0.9800	C5—H5C	0.9800
C1—H1B	0.9800	C6—H6A	0.9800
C1—H1C	0.9800	C6—H6B	0.9800
C2—H2A	0.9800	C6—H6C	0.9800
C2—H2B	0.9800	C7—H7A	0.9800
C2—H2C	0.9800	C7—H7B	0.9800
C3—H3A	0.9800	C7—H7C	0.9800
C3—H3B	0.9800	C8—H8A	0.9800
C3—H3C	0.9800	C8—H8B	0.9800
C4—H4A	0.9800	C8—H8C	0.9800
Cl4—Cu1—Cl1	99.33 (6)	N1—C4—H4C	109.5
Cl4—Cu1—Cl3	133.69 (7)	H4A—C4—H4C	109.5
Cl1—Cu1—Cl3	98.64 (6)	H4B—C4—H4C	109.5
Cl4—Cu1—Cl2	98.44 (7)	C8—N2—C7	109.7 (5)

Cl1—Cu1—Cl2	133.48 (6)	C8—N2—C6	109.5 (5)
Cl3—Cu1—Cl2	99.32 (6)	C7—N2—C6	109.1 (5)
C1—N1—C3	108.6 (5)	C8—N2—C5	109.2 (4)
C1—N1—C2	110.9 (5)	C7—N2—C5	108.5 (5)
C3—N1—C2	109.2 (5)	C6—N2—C5	110.8 (5)
C1—N1—C4	109.7 (5)	N2—C5—H5A	109.5
C3—N1—C4	109.6 (5)	N2—C5—H5B	109.5
C2—N1—C4	108.9 (5)	H5A—C5—H5B	109.5
N1—C1—H1A	109.5	N2—C5—H5C	109.5
N1—C1—H1B	109.5	H5A—C5—H5C	109.5
H1A—C1—H1B	109.5	H5B—C5—H5C	109.5
N1—C1—H1C	109.5	N2—C6—H6A	109.5
H1A—C1—H1C	109.5	N2—C6—H6B	109.5
H1B—C1—H1C	109.5	H6A—C6—H6B	109.5
N1—C2—H2A	109.5	N2—C6—H6C	109.5
N1—C2—H2B	109.5	H6A—C6—H6C	109.5
H2A—C2—H2B	109.5	H6B—C6—H6C	109.5
N1—C2—H2C	109.5	N2—C7—H7A	109.5
H2A—C2—H2C	109.5	N2—C7—H7B	109.5
H2B—C2—H2C	109.5	H7A—C7—H7B	109.5
N1—C3—H3A	109.5	N2—C7—H7C	109.5
N1—C3—H3B	109.5	H7A—C7—H7C	109.5
H3A—C3—H3B	109.5	H7B—C7—H7C	109.5
N1—C3—H3C	109.5	N2—C8—H8A	109.5
H3A—C3—H3C	109.5	N2—C8—H8B	109.5
H3B—C3—H3C	109.5	H8A—C8—H8B	109.5
N1—C4—H4A	109.5	N2—C8—H8C	109.5
N1—C4—H4B	109.5	H8A—C8—H8C	109.5
H4A—C4—H4B	109.5	H8B—C8—H8C	109.5

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1C···Cl2[i]	0.98	2.69	3.585 (7)	153
C2—H2A···Cl1[ii]	0.98	2.79	3.675 (7)	151
C2—H2A···Cl3[ii]	0.98	2.80	3.555 (7)	134
C2—H2B···Cl1[i]	0.98	2.79	3.674 (7)	150
C3—H3B···Cl4	0.98	2.74	3.670 (7)	159
C4—H4A···Cl3[iii]	0.98	2.59	3.555 (7)	166
C5—H5A···Cl2[iv]	0.98	2.68	3.635 (7)	165
C5—H5B···Cl3[v]	0.98	2.81	3.587 (6)	137
C5—H5C···Cl4[i]	0.98	2.63	3.610 (6)	173
C8—H8B···Cl1[iii]	0.98	2.76	3.650 (6)	151
C8—H8C···Cl2[v]	0.98	2.82	3.763 (7)	162

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