



Crystal structure of 1-[2-(diethylazan-iumyl)ethyl]-3-methylimidazolium tetrachloridocuprate(II)

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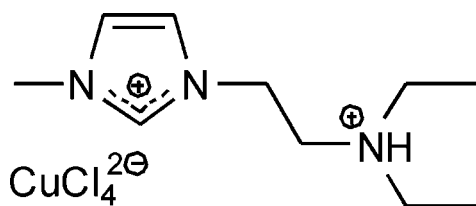
The title compound, (C₁₀H₂₁N₃)[CuCl₄], is composed of one 1-[2-(diethylazan-iumyl)ethyl]-3-methylimidazolium dication and a tetrachloridocuprate(II) dianion. The anion adopts a distorted tetrahedral geometry. Bifurcated interionic N—H...Cl hydrogen bonds and several C—H...Cl contacts are observed, leading to a layer-like arrangement of the components parallel to (100).

Keywords: crystal structure; copper(II) complex; tetrachloridocuprate; 1-[2-(diethylazan-iumyl)ethyl]-3-methylimidazolium dication; hydrogen bonding.

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1. Related literature

For structures of related tetrachloridocuprates(II), see: Russell & Wallwork (1969); Główska & Gilli (1989); Choi *et al.* (2002); Sun & Qu (2005); Elangovan *et al.* (2007*a,b*); Strasser *et al.* (2007). For details of the synthesis, see: Laus *et al.* (2012); Håkansson & Jagner (1990).



2. Experimental

2.1. Crystal data

(C₁₀H₂₁N₃)[CuCl₄]
 $M_r = 388.64$
 Monoclinic, $P2_1/c$
 $a = 17.0041$ (8) Å
 $b = 7.1161$ (6) Å
 $c = 14.4143$ (7) Å
 $\beta = 112.956$ (6)°
 $V = 1606.04$ (17) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.01$ mm⁻¹
 $T = 173$ K
 $0.20 \times 0.16 \times 0.12$ mm

2.2. Data collection

Oxford Diffraction Gemini-R Ultra diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
 $T_{\min} = 0.875$, $T_{\max} = 1$
 10390 measured reflections
 2991 independent reflections
 2361 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.056$
 $S = 0.98$
 2991 reflections
 166 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—Cl4	2.2267 (7)	Cu1—Cl2	2.2456 (8)
Cu1—Cl3	2.2447 (6)	Cu1—Cl1	2.2644 (7)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3N...Cl1	0.93	2.29	3.134 (2)	150
N3—H3N...Cl3	0.93	2.79	3.399 (2)	124
C2—H2...Cl4 ⁱ	0.95	2.66	3.480 (3)	145
C3—H3...Cl2 ⁱⁱ	0.95	2.75	3.423 (3)	128
C3—H3...Cl3 ⁱⁱ	0.95	2.77	3.537 (3)	138
C4—H4...Cl2 ⁱⁱⁱ	0.95	2.84	3.608 (3)	139
C9—H9A...Cl1 ⁱⁱⁱ	0.99	2.78	3.617 (3)	143

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: FF2135).

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supporting information

Acta Cryst. (2015). E71, m110–m111 [https://doi.org/10.1107/S2056989015006799]

Crystal structure of 1-[2-(diethylazaniumyl)ethyl]-3-methylimidazolium tetrachloridocuprate(II)

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S1. Comment

1-[2-(Diethylazaniumyl)ethyl]-3-methylimidazolium ions in deprotonated form can act as bidentate ligands (Laus *et al.*, 2012). In this work, it is shown that they are also capable of coordinating in protonated form. The structure of the ion pair of 3-(2-(diethylammonio)ethyl)-1-methylimidazolium tetrachlorocuprate (II) is shown in Figure 1. The anion adopts a distorted tetrahedral geometry. The Cl—Cu—Cl angles range from 97° to 134°. The heterocyclic rings of the cation are oriented parallel to the (3 7 2) and (3 $\bar{7}$ 2) planes with an interplanar angle of 32.5°. The side chain is twisted out of the heterocyclic ring plane. In the crystal structure, the cations and anions are linked by N—H···Cl and C—H···Cl hydrogen bonds (Figure 2).

S2. Experimental

The title compound, (C₁₀H₂₁N₃)CuCl₄, was obtained from the reaction of bis-(1-(2-(diethylamino)ethyl)-3-methylimidazolin-2-ylidene) di-silver(I) bis(bis(triflimide)) (Laus *et al.*, 2012) and carbonyl chlorocopper(I) (Håkansson & Jagner, 1990) in methanol under ambient conditions. This unconventional synthesis involves redox, protonation and complexation steps. Yellow-green single crystals were obtained from MeOH in modest yield. Melting point 118–120 °C.

S3. Refinement

All hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{parent atom})$.

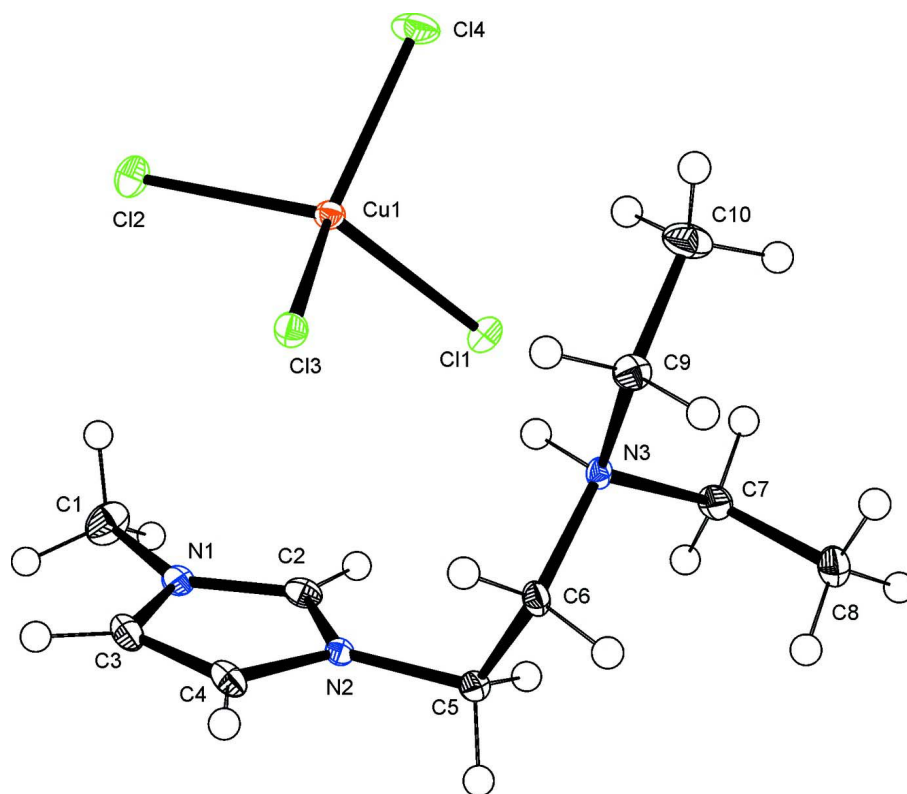


Figure 1

Ion pair of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

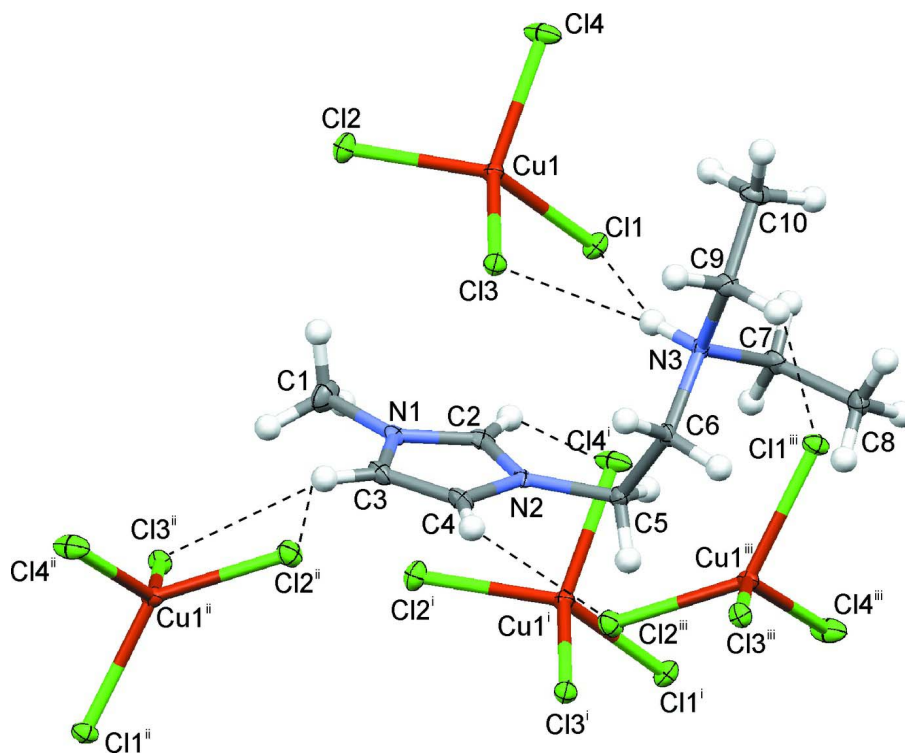


Figure 2

Interionic contacts in the crystal structure of the title compound. Symmetry codes: (i) $x, -1 + y, z$; (ii) $-x, -1/2 + y, 3/2 - z$; (iii) $x, 1/2 - y, 1/2 + z$.

1-[2-(Diethylazaniumyl)ethyl]-3-methylimidazolium tetrachloridocuprate(II)

Crystal data

$(C_{10}H_{21}N_3)[CuCl_4]$
 $M_r = 388.64$
 Monoclinic, $P2_1/c$
 $a = 17.0041 (8) \text{ \AA}$
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 $\beta = 112.956 (6)^\circ$
 $V = 1606.04 (17) \text{ \AA}^3$
 $Z = 4$

$F(000) = 796$
 $D_x = 1.607 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 4805 reflections
 $\theta = 3.1\text{--}28.5^\circ$
 $\mu = 2.01 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 Fragment, yellow
 $0.20 \times 0.16 \times 0.12 \text{ mm}$

Data collection

Oxford Diffraction Gemini-R Ultra
 diffractometer
 Graphite monochromator
 Detector resolution: $10.3822 \text{ pixels mm}^{-1}$
 ω (1° width) scans
 Absorption correction: multi-scan
 (*CrysAlis PRO*; Oxford Diffraction, 2010)
 $T_{\min} = 0.875, T_{\max} = 1$

10390 measured reflections
 2991 independent reflections
 2361 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\max} = 25.5^\circ, \theta_{\min} = 3.1^\circ$
 $h = -20 \rightarrow 20$
 $k = -6 \rightarrow 8$
 $l = -17 \rightarrow 17$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.056$ $S = 0.98$

2991 reflections

166 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0234P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$ *Special details***Experimental.** Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.**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 (\AA^2)*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.24089 (2)	0.54432 (5)	0.77447 (2)	0.01040 (9)
Cl1	0.33356 (4)	0.30011 (9)	0.81388 (5)	0.01280 (16)
Cl2	0.12793 (4)	0.62361 (10)	0.63485 (5)	0.01575 (16)
Cl3	0.17620 (4)	0.47770 (9)	0.87973 (4)	0.01224 (15)
Cl4	0.33226 (4)	0.76469 (10)	0.76985 (6)	0.02164 (18)
N3	0.34210 (13)	0.2088 (3)	1.03033 (15)	0.0089 (5)
H3N	0.3191	0.2461	0.9632	0.011*
N2	0.16575 (13)	-0.0096 (3)	0.88310 (15)	0.0089 (5)
N1	0.08640 (14)	0.0672 (3)	0.73070 (15)	0.0118 (5)
C9	0.35838 (17)	0.3852 (4)	1.09319 (19)	0.0130 (6)
H9A	0.3812	0.3503	1.1654	0.016*
H9B	0.3036	0.4519	1.0777	0.016*
C2	0.16480 (17)	0.0163 (4)	0.79170 (19)	0.0125 (6)
H2	0.2121	0.0012	0.7729	0.015*
C8	0.46893 (17)	0.0322 (4)	1.15266 (19)	0.0164 (6)
H8A	0.4892	0.1404	1.1978	0.025*
H8B	0.5178	-0.0452	1.1564	0.025*
H8C	0.4301	-0.0429	1.1731	0.025*
C6	0.27576 (16)	0.0917 (4)	1.04753 (19)	0.0105 (6)
H6A	0.2283	0.1748	1.0451	0.013*
H6B	0.3012	0.0373	1.1161	0.013*
C5	0.23917 (16)	-0.0678 (4)	0.97205 (19)	0.0124 (6)
H5A	0.2842	-0.1156	0.9508	0.015*

H5B	0.2219	-0.1721	1.0055	0.015*
C7	0.42237 (16)	0.1000 (4)	1.04603 (19)	0.0132 (6)
H7A	0.4613	0.1809	1.0273	0.016*
H7B	0.4074	-0.0098	1.0003	0.016*
C10	0.42071 (19)	0.5163 (4)	1.0745 (2)	0.0193 (7)
H10A	0.4779	0.4604	1.1017	0.029*
H10B	0.4218	0.6369	1.1079	0.029*
H10C	0.4028	0.5367	1.0019	0.029*
C1	0.05856 (19)	0.1108 (4)	0.62341 (19)	0.0215 (7)
H1A	0.0668	0.2451	0.6151	0.032*
H1B	-0.002	0.0793	0.5887	0.032*
H1C	0.0922	0.0373	0.5946	0.032*
C3	0.03637 (17)	0.0745 (4)	0.78593 (19)	0.0138 (6)
H3	-0.0224	0.1072	0.7612	0.017*
C4	0.08539 (16)	0.0273 (4)	0.8808 (2)	0.0134 (6)
H4	0.0682	0.0206	0.9359	0.016*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01055 (17)	0.00944 (18)	0.01216 (18)	-0.00016 (15)	0.00545 (14)	0.00046 (14)
Cl1	0.0154 (4)	0.0136 (4)	0.0110 (3)	0.0043 (3)	0.0068 (3)	0.0018 (3)
Cl2	0.0162 (4)	0.0190 (4)	0.0114 (3)	0.0037 (3)	0.0048 (3)	0.0018 (3)
Cl3	0.0113 (3)	0.0140 (4)	0.0119 (3)	0.0003 (3)	0.0051 (3)	0.0012 (3)
Cl4	0.0185 (4)	0.0115 (4)	0.0420 (5)	-0.0021 (3)	0.0196 (4)	-0.0007 (3)
N3	0.0081 (12)	0.0116 (12)	0.0062 (11)	0.0000 (10)	0.0020 (10)	0.0009 (9)
N2	0.0094 (12)	0.0063 (13)	0.0093 (11)	-0.0013 (9)	0.0017 (10)	-0.0026 (9)
N1	0.0130 (12)	0.0092 (13)	0.0098 (12)	-0.0028 (10)	0.0007 (10)	-0.0026 (9)
C9	0.0158 (15)	0.0119 (15)	0.0110 (14)	-0.0007 (12)	0.0049 (12)	-0.0017 (11)
C2	0.0153 (15)	0.0090 (15)	0.0138 (15)	-0.0033 (12)	0.0063 (13)	-0.0046 (11)
C8	0.0107 (14)	0.0169 (16)	0.0182 (15)	0.0005 (13)	0.0020 (12)	0.0005 (13)
C6	0.0070 (14)	0.0142 (16)	0.0101 (14)	-0.0004 (11)	0.0029 (12)	0.0007 (11)
C5	0.0095 (14)	0.0109 (16)	0.0163 (15)	0.0002 (12)	0.0045 (12)	0.0023 (12)
C7	0.0092 (14)	0.0142 (16)	0.0184 (15)	0.0006 (12)	0.0079 (12)	0.0011 (12)
C10	0.0273 (17)	0.0147 (17)	0.0151 (15)	-0.0083 (13)	0.0075 (13)	-0.0039 (12)
C1	0.0277 (18)	0.0217 (18)	0.0119 (15)	0.0021 (14)	0.0044 (14)	0.0009 (13)
C3	0.0098 (14)	0.0136 (17)	0.0179 (15)	-0.0019 (12)	0.0055 (13)	-0.0039 (12)
C4	0.0106 (14)	0.0146 (15)	0.0165 (15)	-0.0034 (12)	0.0070 (13)	-0.0037 (12)

Geometric parameters (Å, °)

Cu1—Cl4	2.2267 (7)	C8—H8A	0.98
Cu1—Cl3	2.2447 (6)	C8—H8B	0.98
Cu1—Cl2	2.2456 (8)	C8—H8C	0.98
Cu1—Cl1	2.2644 (7)	C6—C5	1.527 (4)
N3—C6	1.499 (3)	C6—H6A	0.99
N3—C7	1.507 (3)	C6—H6B	0.99
N3—C9	1.509 (3)	C5—H5A	0.99

N3—H3N	0.93	C5—H5B	0.99
N2—C2	1.324 (3)	C7—H7A	0.99
N2—C4	1.379 (3)	C7—H7B	0.99
N2—C5	1.458 (3)	C10—H10A	0.98
N1—C2	1.329 (3)	C10—H10B	0.98
N1—C3	1.374 (3)	C10—H10C	0.98
N1—C1	1.463 (3)	C1—H1A	0.98
C9—C10	1.513 (4)	C1—H1B	0.98
C9—H9A	0.99	C1—H1C	0.98
C9—H9B	0.99	C3—C4	1.337 (4)
C2—H2	0.95	C3—H3	0.95
C8—C7	1.508 (4)	C4—H4	0.95
C14—Cu1—C13	134.47 (3)	C5—C6—H6A	108.6
C14—Cu1—C12	99.16 (3)	N3—C6—H6B	108.6
C13—Cu1—C12	100.69 (3)	C5—C6—H6B	108.6
C14—Cu1—C11	97.04 (3)	H6A—C6—H6B	107.5
C13—Cu1—C11	98.33 (3)	N2—C5—C6	112.7 (2)
C12—Cu1—C11	133.31 (3)	N2—C5—H5A	109
C6—N3—C7	112.7 (2)	C6—C5—H5A	109
C6—N3—C9	109.68 (18)	N2—C5—H5B	109
C7—N3—C9	113.2 (2)	C6—C5—H5B	109
C6—N3—H3N	107	H5A—C5—H5B	107.8
C7—N3—H3N	107	N3—C7—C8	113.7 (2)
C9—N3—H3N	107	N3—C7—H7A	108.8
C2—N2—C4	108.8 (2)	C8—C7—H7A	108.8
C2—N2—C5	126.0 (2)	N3—C7—H7B	108.8
C4—N2—C5	125.19 (19)	C8—C7—H7B	108.8
C2—N1—C3	108.4 (2)	H7A—C7—H7B	107.7
C2—N1—C1	125.8 (2)	C9—C10—H10A	109.5
C3—N1—C1	125.9 (2)	C9—C10—H10B	109.5
N3—C9—C10	112.5 (2)	H10A—C10—H10B	109.5
N3—C9—H9A	109.1	C9—C10—H10C	109.5
C10—C9—H9A	109.1	H10A—C10—H10C	109.5
N3—C9—H9B	109.1	H10B—C10—H10C	109.5
C10—C9—H9B	109.1	N1—C1—H1A	109.5
H9A—C9—H9B	107.8	N1—C1—H1B	109.5
N2—C2—N1	108.4 (2)	H1A—C1—H1B	109.5
N2—C2—H2	125.8	N1—C1—H1C	109.5
N1—C2—H2	125.8	H1A—C1—H1C	109.5
C7—C8—H8A	109.5	H1B—C1—H1C	109.5
C7—C8—H8B	109.5	C4—C3—N1	107.6 (2)
H8A—C8—H8B	109.5	C4—C3—H3	126.2
C7—C8—H8C	109.5	N1—C3—H3	126.2
H8A—C8—H8C	109.5	C3—C4—N2	106.8 (2)
H8B—C8—H8C	109.5	C3—C4—H4	126.6
N3—C6—C5	114.8 (2)	N2—C4—H4	126.6
N3—C6—H6A	108.6		

C6—N3—C9—C10	-176.3 (2)	C4—N2—C5—C6	-72.8 (3)
C7—N3—C9—C10	56.9 (3)	N3—C6—C5—N2	-88.4 (3)
C4—N2—C2—N1	-0.5 (3)	C6—N3—C7—C8	-63.9 (3)
C5—N2—C2—N1	179.5 (2)	C9—N3—C7—C8	61.3 (3)
C3—N1—C2—N2	0.4 (3)	C2—N1—C3—C4	-0.1 (3)
C1—N1—C2—N2	179.5 (2)	C1—N1—C3—C4	-179.2 (2)
C7—N3—C6—C5	-65.8 (3)	N1—C3—C4—N2	-0.2 (3)
C9—N3—C6—C5	167.1 (2)	C2—N2—C4—C3	0.4 (3)
C2—N2—C5—C6	107.2 (3)	C5—N2—C4—C3	-179.5 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3 <i>N</i> ...C11	0.93	2.29	3.134 (2)	150
N3—H3 <i>N</i> ...C13	0.93	2.79	3.399 (2)	124
C2—H2...C14 ⁱ	0.95	2.66	3.480 (3)	145
C3—H3...C12 ⁱⁱ	0.95	2.75	3.423 (3)	128
C3—H3...C13 ⁱⁱ	0.95	2.77	3.537 (3)	138
C4—H4...C12 ⁱⁱⁱ	0.95	2.84	3.608 (3)	139
C9—H9 <i>A</i> ...C11 ⁱⁱⁱ	0.99	2.78	3.617 (3)	143

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, y-1/2, -z+3/2$; (iii) $x, -y+1/2, z+1/2$.