Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

μ_3-Chlorido-tris(bis{1-[2-(dimethyl-amino)ethyl]-3-methylimidazol-2-yl-idene}silver(I)) dichloride

Christoph Topf, Sebastian Leitner and Uwe Monkowius*

Johannes Kepler Universität Linz, Institut für Anorganische Chemie, Altenberger-strasse 69, A-4040 Linz, Austria
Correspondence e-mail: uwe.monkowius@jku.at

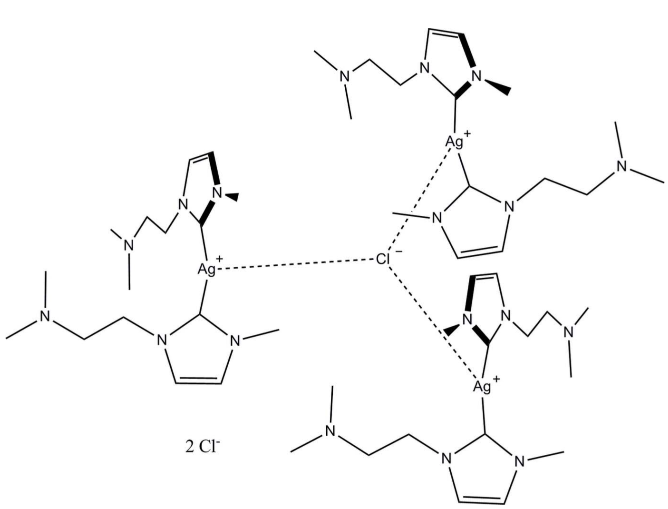
Received 31 January 2012; accepted 2 February 2012

Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.005 Å; R factor = 0.034; wR factor = 0.095; data-to-parameter ratio = 16.5.

In the crystal structure of the title compound, $[Ag_3Cl(C_8H_{15}N_3)_6]Cl_2$, the Ag^I ion, which is located on a twofold rotation axis, exists in a T-shape coordination environment. Two carbene C atoms of the N-heterocyclic carbene (NHC) ligands are bonded tightly forming a slightly bent $[Ag(NHC)_2]^+$ cation [C—Ag—C angle = 162.80 (18)°]. Three of these complex cations are further aggregated by one bridging chloride anion, which is lying on a threefold rotoinversion axis and is only loosely binding to the Ag^+ ions. The N atom of the amine group is not engaged in any coordinative bond.

Related literature

For related literature concerning similar N-heterocyclic carbenes, see: Topf, Hirtenlehner, Fleck *et al.* (2011); Topf, Hirtenlehner & Monkowius (2011); Leitner *et al.* (2011). For related structures, see: Hirtenlehner *et al.* (2011); Wang *et al.* (2006). For details of the preparation, see: Topf, Hirtenlehner, Zabel *et al.* (2011).



Experimental

Crystal data

$[Ag_3Cl(C_8H_{15}N_3)_6]Cl_2$
M_r = 1349.34
Trigonal, $R\bar{3}c$
a = 12.7300 (16) Å
c = 66.789 (12) Å
V = 9373 (2) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 1.11 mm^{-1}
T = 200 K
0.50 × 0.36 × 0.31 mm

Data collection

Bruker SMART X2S diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.61, T_{max} = 0.73
18593 measured reflections
1859 independent reflections
1590 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.095
S = 1.03
1859 reflections
113 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Data collection: *APEX2* and *GIS* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We thank Professor Günther Knör for fruitful discussion and generous support of the experimental work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5811).

References

Bruker (2009). *APEX2*, *GIS*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Hirtenlehner, C., Krims, C., Hölbling, J., List, M., Zabel, M., Fleck, M., Berger, R. J. F., Schoefberger, W. & Monkowius, U. (2011). *Dalton Trans.* **40**, 9899–9910.
Leitner, S., List, M. & Monkowius, U. (2011). *Z. Naturforsch. Teil B*, **66**, 1255–1260.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Topf, C., Hirtenlehner, C., Fleck, M., List, M. & Monkowius, U. (2011). *Z. Anorg. Allg. Chem.* **637**, 2129–2134.
Topf, C., Hirtenlehner, C. & Monkowius, U. (2011). *J. Organomet. Chem.* **696**, 3274–3278.
Topf, C., Hirtenlehner, C., Zabel, M., List, M., Fleck, M. & Monkowius, U. (2011). *Organometallics*, pp. 2755–2764.
Wang, X., Liu, S., Wenig, L.-H. & Jin, G.-X. (2006). *Organometallics*, **25**, 3565–3569.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supplementary materials

Acta Cryst. (2012). E**68**, m272 [doi:10.1107/S1600536812004473]

μ_3-Chlorido-tris(bis{1-[2-(dimethylamino)ethyl]-3-methylimidazol-2-ylidene}silver(I)) dichloride

Christoph Topf, Sebastian Leitner and Uwe Monkowius

Comment

In the course of our studies on gold- and silver-complexes bearing functionalized N-heterocyclic carbenes (NHCs), we became interested in examples with amino groups containing side arms at a nitrogen atom of the NHC ligands (Topf, Hirtenlehner, Fleck *et al.* (2011); Topf, Hirtenlehner & Monkowius (2011); Leitner *et al.*, 2011; Hirtenlehner *et al.*, 2011). Just recently, we published the multifarious coordination patterns of such silver complexes (Topf, Hirtenlehner, Zabel *et al.*, 2011): E.g., in the ionic compound $[(C_8H_{15}N_3)_2Ag][AgCl_2]$, which is formed from the respective imidazolium chloride and Ag_2O in dichloromethane, the ions are aggregated to infinite chains with short silver-silver contacts. Treatment of this complex with HBF_4 yields the cluster $(C_8H_{15}N_3)_4Ag_{10}Cl_{10}$ with the carbene carbon atom binding in a unusual μ_2-fashion to two silver atoms. In an attempt to prepare this cluster, crystals of the title compound were formed representing the third silver chloride complex in the series of this ligand. The formation of this complex is easily rationalized by the precipitation of AgCl from $[(C_8H_{15}N_3)_2Ag][AgCl_2]$ in solution.

The silver atom is in a slightly bent linear coordination with an Ag1—C1 bond length of 2.099 (3) Å and an angle C1—Ag1—C1^i of 162.8 (2)°. Perpendicular to the C1—Ag1—C1^i vector, a chloride anion is loosely binding with an Ag1—Cl1 bond length of 2.981 (1) Å. The chloride Cl1 is linking three $[(C_8H_{15}N_3)_2Ag]^+$ units in a μ_3-fashion forming a D_3 symmteric trimeric aggregate. The net 2+ charge is balanced by two non-interacting chloride ions. Within other cationic species of the type $[(NHC)_2Ag]^+$, the imidazole ring planes are usually found in a coplanar arrangement due to a higher π-backbonding contribution compared to a perpendicular orientation. Presumably because of steric reasons, the $[(C_8H_{15}N_3)_2Ag]^+$ moiety features an arrangement with both imidazole ring planes approaching a perpendicular orientation [N1—C1—C1^i—N1^i 89.8°]. The distance between two silver atoms within the trimer is 5.164 Å, which is well beyond the range of argentophilic interactions. It should be noted, that this aggregation pattern is very rare and to the best of our knowledge reported only for $\{[(NHC)_2Ag]_3(\mu_3\text{-I})\}I_2$ (NHC = 1-methyl-3-picolyl-imidazol-2-ylidene) (Wang *et al.*, 2006) and $\{[(NHC)_2Au]_3(\mu_3\text{-Br})\}Br_2$ (NHC= 1-methyl-3-benzyl-imidazol-2-ylidene) (Hirtenlehner *et al.*, 2011).

Experimental

Crystals of the title compound were formed in an attempt to synthesize the silver cluster $(C_8H_{15}N_3)_4Ag_{10}Cl_{10}$ according to a literature procedure (Topf, Hirtenlehner, Zabel *et al.*, 2011).

Refinement

The hydrogen atoms were placed in calculated positions with C—H = 0.95–0.99 Å and refined using a riding model with U_{iso}(H) = 1.5 U_{eq}(C) for methyl groups and U_{iso}(H) = 1.2 U_{eq}(C) for methylen and aromatic hydrogen atoms. The highest residual electron density peak is located 1.28 Å from H9A and the deepest hole is located 0.53 Å from C9.

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

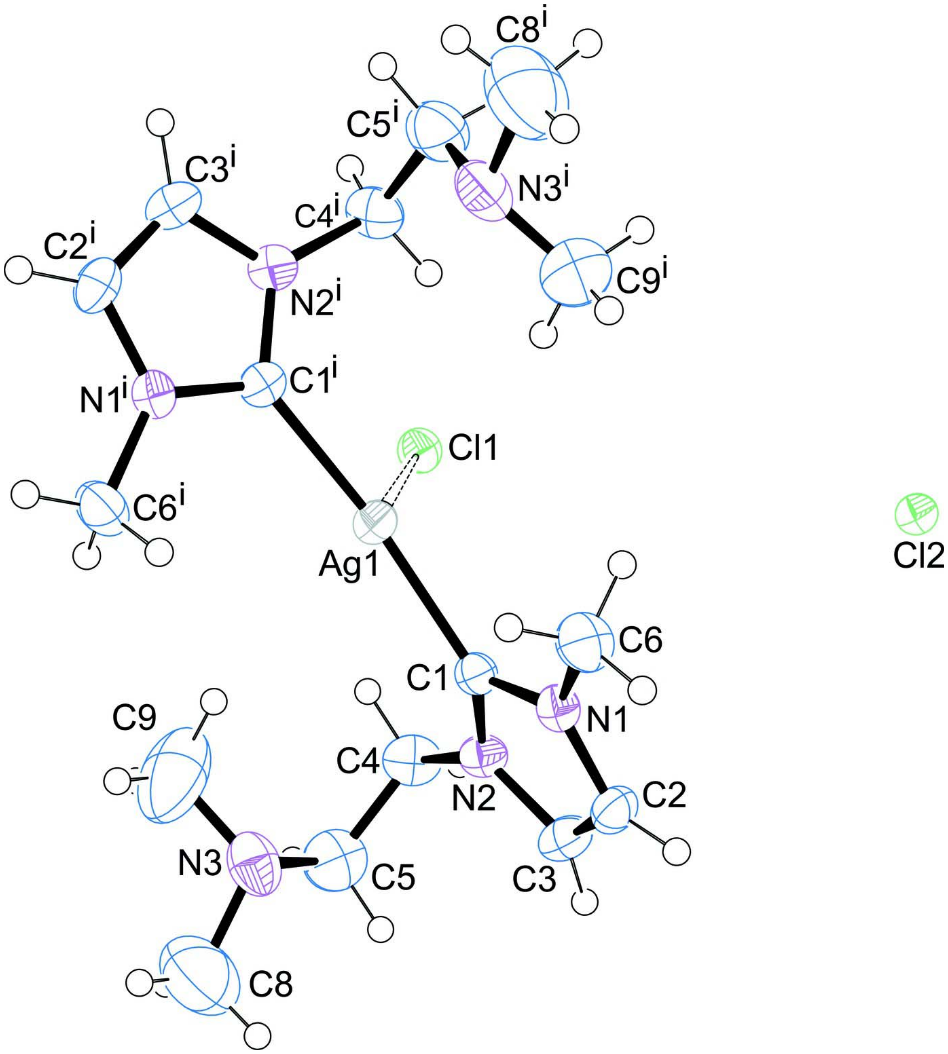


Figure 1

View of the title compound with the atom numbering scheme (symmetry code: (i) *x*-*y* + 1/3, -*y* + 2/3, -*z* + 1/6). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

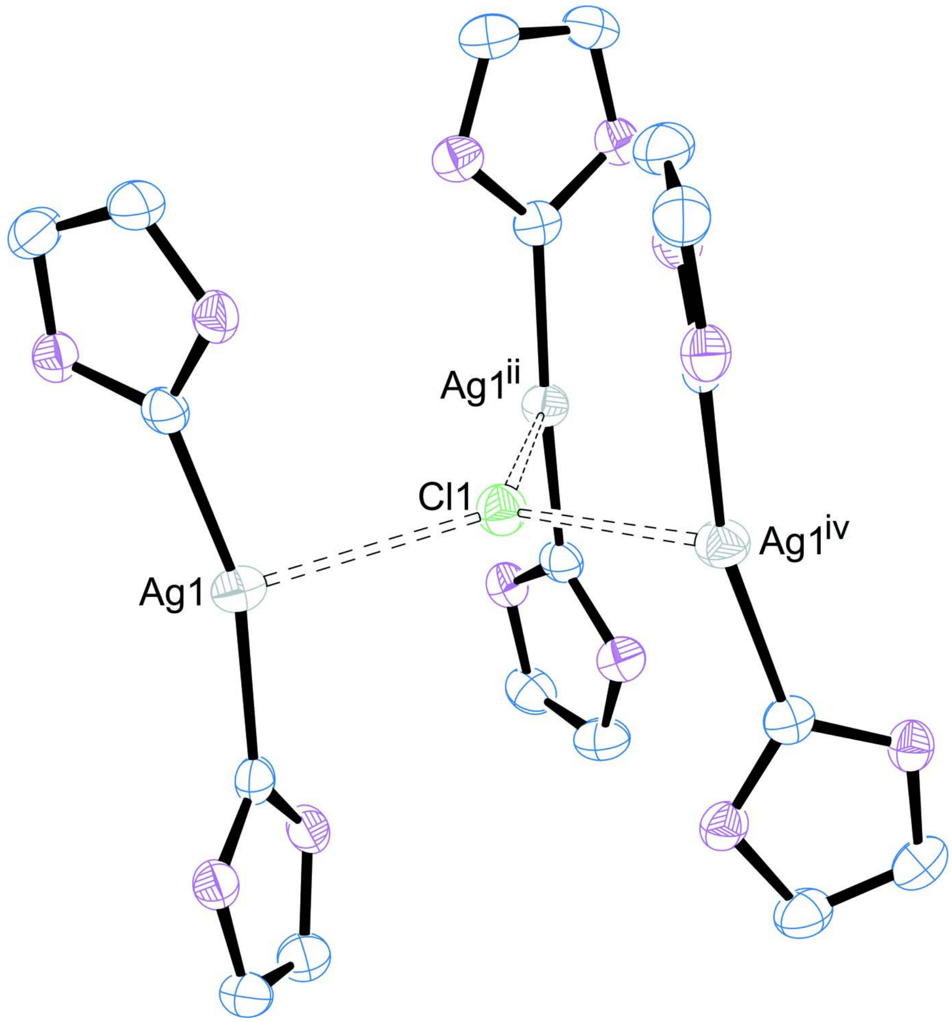


Figure 2

$[Ag_3Cl]^{2+}$ cation in the crystals of the title compound. The H atoms and the methyl and 2-dimethyl-amino-ethyl groups are omitted for the sake of clarity (symmetry codes: (ii) $-y + 1, x-y, z$; (iv) $y + 1/3, x - 1/3, -z + 1/6$).

μ_3-Chlorido-tris(bis{1-[2-(dimethylamino)ethyl]-3-methylimidazol-2- ylidene}silver(I)) dichloride

Crystal data

$[Ag_3Cl(C_8H_{15}N_3)_2]Cl_2$	$F(000) = 4176$
$M_r = 1349.34$	$D_x = 1.434$ Mg m^{-3}
Trigonal, $R\bar{3}c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.7300$ (16) Å	$\mu = 1.11$ mm^{-1}
$c = 66.789$ (12) Å	$T = 200$ K
$V = 9373$ (2) Å^3	Prism, colourless
$Z = 6$	$0.50 \times 0.36 \times 0.31$ mm

Data collection

Bruker SMART X2S diffractometer	ω scans
Radiation source: sealed MicroFocus tube	Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
Doubly curved silicon crystal monochromator	$T_{min} = 0.61$, $T_{max} = 0.73$

18593 measured reflections
1859 independent reflections
1590 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

θ_{max} = 25.1°, θ_{min} = 3.1°
$h = -15 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -79 \rightarrow 79$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.095$
$S = 1.03$
1859 reflections
113 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 47.4314P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.28$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ 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.

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ag1	0.90085 (3)	0.3333	0.0833	0.03038 (16)
C6	1.1504 (3)	0.5164 (4)	0.05466 (6)	0.0422 (9)
H6A	1.1374	0.5764	0.0617	0.063*
H6B	1.2184	0.558	0.0453	0.063*
H6C	1.1689	0.4703	0.0644	0.063*
C1	0.9354 (3)	0.3530 (3)	0.05243 (5)	0.0257 (7)
N2	0.8610 (3)	0.2965 (3)	0.03679 (4)	0.0284 (6)
C5	0.7252 (4)	0.0798 (4)	0.03044 (7)	0.0543 (11)
H5A	0.6394	0.0146	0.0315	0.065*
H5B	0.7471	0.0909	0.0161	0.065*
N1	1.0411 (2)	0.4340 (2)	0.04359 (4)	0.0271 (6)
C4	0.7366 (3)	0.1961 (4)	0.03843 (6)	0.0388 (9)
H4A	0.682	0.2158	0.0308	0.047*
H4B	0.7112	0.1848	0.0526	0.047*
C3	0.9192 (3)	0.3417 (3)	0.01870 (6)	0.0358 (9)
H3	0.8853	0.3163	0.0057	0.043*
C2	1.0327 (3)	0.4284 (3)	0.02306 (5)	0.0341 (8)
H2	1.095	0.4766	0.0138	0.041*
N3	0.8016 (3)	0.0410 (3)	0.04089 (6)	0.0475 (9)
C8	0.7953 (7)	−0.0580 (6)	0.02927 (11)	0.101 (2)
H8A	0.842	−0.0898	0.036	0.151*
H8B	0.829	−0.0286	0.0159	0.151*

H8C	0.7104	−0.1226	0.028	0.151*
C9	0.7645 (7)	0.0065 (6)	0.06074 (11)	0.114 (3)
H9A	0.772	0.0761	0.0682	0.172*
H9B	0.8157	−0.0217	0.067	0.172*
H9C	0.6797	−0.0591	0.0609	0.172*
Cl1	0.6667	0.3333	0.0833	0.0307 (4)
Cl2	0.3333	0.6667	0.00857 (2)	0.0344 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0353 (2)	0.0290 (2)	0.0247 (2)	0.01451 (11)	0.00056 (7)	0.00112 (14)
C6	0.032 (2)	0.035 (2)	0.048 (2)	0.0078 (17)	−0.0022 (17)	−0.0035 (17)
C1	0.0288 (17)	0.0288 (17)	0.0267 (18)	0.0197 (15)	−0.0005 (14)	0.0007 (13)
N2	0.0256 (14)	0.0345 (16)	0.0289 (16)	0.0180 (13)	0.0007 (12)	−0.0018 (12)
C5	0.040 (2)	0.053 (3)	0.057 (3)	0.013 (2)	−0.003 (2)	−0.005 (2)
N1	0.0246 (14)	0.0259 (14)	0.0314 (15)	0.0131 (12)	0.0013 (11)	0.0016 (12)
C4	0.0238 (18)	0.046 (2)	0.044 (2)	0.0161 (17)	−0.0016 (15)	−0.0062 (18)
C3	0.040 (2)	0.048 (2)	0.0245 (19)	0.0255 (18)	0.0000 (15)	0.0000 (15)
C2	0.039 (2)	0.039 (2)	0.0290 (19)	0.0233 (17)	0.0095 (15)	0.0072 (15)
N3	0.0411 (19)	0.0327 (18)	0.061 (2)	0.0126 (15)	−0.0096 (17)	−0.0030 (16)
C8	0.108 (5)	0.066 (4)	0.121 (6)	0.039 (4)	0.011 (4)	−0.010 (4)
C9	0.132 (7)	0.081 (5)	0.069 (4)	0.007 (4)	−0.034 (4)	0.012 (3)
Cl1	0.0299 (6)	0.0299 (6)	0.0323 (10)	0.0150 (3)	0	0
Cl2	0.0356 (5)	0.0356 (5)	0.0319 (7)	0.0178 (3)	0	0

Geometric parameters (Å, º)

Ag1—C1^{i}	2.099 (3)	N1—C2	1.374 (5)
Ag1—C1	2.099 (3)	C4—H4A	0.99
C6—N1	1.458 (5)	C4—H4B	0.99
C6—H6A	0.98	C3—C2	1.340 (5)
C6—H6B	0.98	C3—H3	0.95
C6—H6C	0.98	C2—H2	0.95
C1—N2	1.350 (5)	N3—C9	1.402 (8)
C1—N1	1.355 (4)	N3—C8	1.447 (7)
N2—C3	1.383 (5)	C8—H8A	0.98
N2—C4	1.459 (5)	C8—H8B	0.98
C5—N3	1.469 (6)	C8—H8C	0.98
C5—C4	1.511 (6)	C9—H9A	0.98
C5—H5A	0.99	C9—H9B	0.98
C5—H5B	0.99	C9—H9C	0.98
C1^{i}—Ag1—C1	162.80 (18)	N2—C4—H4B	109.4
N1—C6—H6A	109.5	C5—C4—H4B	109.4
N1—C6—H6B	109.5	H4A—C4—H4B	108.0
H6A—C6—H6B	109.5	C2—C3—N2	106.6 (3)
N1—C6—H6C	109.5	C2—C3—H3	126.7
H6A—C6—H6C	109.5	N2—C3—H3	126.7
H6B—C6—H6C	109.5	C3—C2—N1	106.5 (3)

N2—C1—N1	103.5 (3)	C3—C2—H2	126.8
N2—C1—Ag1	130.4 (3)	N1—C2—H2	126.8
N1—C1—Ag1	126.0 (2)	C9—N3—C8	111.8 (5)
C1—N2—C3	111.5 (3)	C9—N3—C5	112.2 (5)
C1—N2—C4	125.0 (3)	C8—N3—C5	106.3 (4)
C3—N2—C4	123.4 (3)	N3—C8—H8A	109.5
N3—C5—C4	114.0 (3)	N3—C8—H8B	109.5
N3—C5—H5A	108.8	H8A—C8—H8B	109.5
C4—C5—H5A	108.8	N3—C8—H8C	109.5
N3—C5—H5B	108.8	H8A—C8—H8C	109.5
C4—C5—H5B	108.8	H8B—C8—H8C	109.5
H5A—C5—H5B	107.7	N3—C9—H9A	109.5
C1—N1—C2	111.9 (3)	N3—C9—H9B	109.5
C1—N1—C6	123.7 (3)	H9A—C9—H9B	109.5
C2—N1—C6	124.4 (3)	N3—C9—H9C	109.5
N2—C4—C5	111.3 (3)	H9A—C9—H9C	109.5
N2—C4—H4A	109.4	H9B—C9—H9C	109.5
C5—C4—H4A	109.4		

Symmetry code: (i) $x-y+1/3$, $-y+2/3$, $-z+1/6$.