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trans-Dichloridotetrapyrazine-ruthenium(II) dichloromethane disolvate

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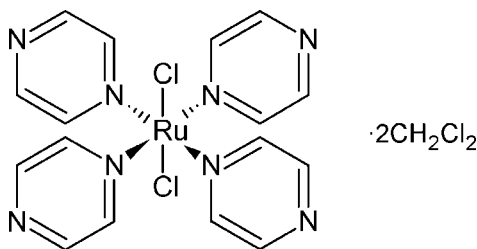
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.016; wR factor = 0.040; data-to-parameter ratio = 17.3.

In the title compound, $[\text{RuCl}_2(\text{C}_4\text{H}_4\text{N}_2)_4] \cdot 2\text{CH}_2\text{Cl}_2$, the Ru^{II} atom occupies a position of 222 symmetry and the C atom of the solvent molecule occupies a site with twofold symmetry. The Ru^{II} atom has a slightly distorted octahedral geometry. The pyrazine rings are propeller-like and rotated $45.1(1)^\circ$ from the RuN_4 plane. In the crystal, the complex and solvent molecules are bridged by weak $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds along the c axis. Weak intermolecular $\text{C}-\text{H} \cdots \text{Cl}$ contacts link the complexes in the ab plane, forming a network.

Related literature

The synthesis of the title complex and its use as a building block in coordination networks are described by Carlucci *et al.* (2002) and Coe (2004). For related structures using pyridine and varying *trans* ligands, see: Coe *et al.* (1995); Desjardins *et al.* (1999).



Experimental

Crystal data

 $[\text{RuCl}_2(\text{C}_4\text{H}_4\text{N}_2)_4] \cdot 2\text{CH}_2\text{Cl}_2$
 $M_r = 662.19$
 Tetragonal, $I4_122$
 $a = 7.3059(2)$ Å
 $c = 47.3659(16)$ Å
 $V = 2528.21(14)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.28$ mm⁻¹
 $T = 100$ K
 $0.10 \times 0.10 \times 0.08$ mm

Data collection

 Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1996)
 $T_{\text{min}} = 0.882$, $T_{\text{max}} = 0.908$

 15409 measured reflections
 1399 independent reflections
 1363 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.040$
 $S = 1.03$
 1399 reflections
 81 parameters
 H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 1.01$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³
 Absolute structure: Flack (1983),
 508 Friedel pairs
 Flack parameter: 0.26 (4)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{C3}-\text{H3A} \cdots \text{Cl1}^{\text{i}}$	0.95	2.88	3.555 (2)	129
$\text{C5}-\text{H5A} \cdots \text{N2}^{\text{ii}}$	0.92 (2)	2.46 (2)	3.338 (2)	158 (2)

 Symmetry codes: (i) $-x + 1, -y + 1, z$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{4}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; 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: *SHELXTL*.

We thank Austin College (Cullen Funds) for supporting innovative undergraduate education and the Welch Foundation (AD-0007) for a chemistry department grant furthering undergraduate research. We also recognize the work of Jessie H. Berger, Tehreem Bilal, Michela L. Brumfield, Raven M. Clark, Edward J. Selvik, Jacob B. Smith, and Hans H. Yoon, who, as fellow students with WK and AER in an advanced inorganic lab, synthesized and attempted to grow crystals of the title compound.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5139).

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supporting information

Acta Cryst. (2012). E68, m1193 [doi:10.1107/S1600536812035817]

***trans*-Dichloridotetrapyrazineruthenium(II) dichloromethane disolvate**

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S1. Comment

The pyrazine ligands are rotated $45.1(1)^\circ$ from the N—Ru—N plane (Fig. 1) consistent with other propeller-like structures (Coe *et al.*, 1995 and references therein). The terminal chloride atoms on the $\text{Ru}(\text{pz})_4\text{Cl}_2$ complexes are 2.86 - 2.94 Å from the four hydrogen atoms belonging to neighboring pyrazine groups (Fig. 2). This additional interaction enhances the stability of the propeller-like structure.

The Ru—Cl bond length is 2.3920 (5) Å and the Ru—N bond length is 2.0620 (14) Å. These distances are on the low side of the narrow range of bond lengths when this complex is used in supramolecular assemblies (Carlucci *et al.*, 2002), indicating very little influence on bond distance upon further coordination of this metal-based building block. Ru—N distances in tetrakis(pyridine) RuL_2 , are 2.09 Å ($L = 2$ -chlorophenylcyanamide) (Desjardins, *et al.*, 1999), or 2.08 Å ($L =$ one chloride and one benzonitrile) (Coe *et al.*, 1995).

H-bonds and intermolecular contacts form a network in the crystal. Atom Cl11 has an intermolecular contact with a hydrogen atom on two pyrazine ligands on a neighboring complex (Fig. 3 and Table 1). At the same time, the hydrogen atoms of the dichloromethane solvate have weak hydrogen bonds between two terminal N-atoms on the pyrazine ligands of two separate $\text{Ru}(\text{pz})_4\text{Cl}_2$ complexes (Fig. 4 and Table 1). Additionally, the solvent chloride atom is 3.383 (3) Å from the C2 atom near the uncoordinated nitrogen on the pyrazine ligand.

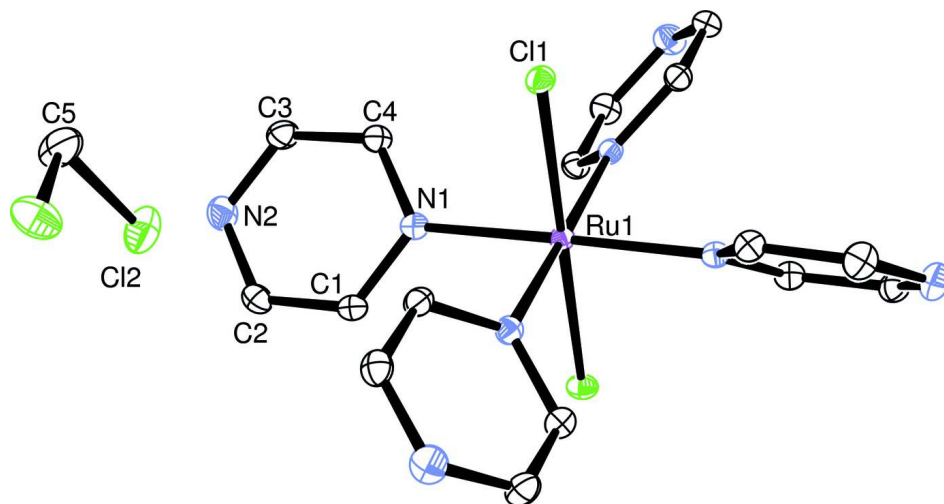
S2. Experimental

The ruthenium complex was synthesized by the student co-authors in the laboratory component of Austin College's advanced inorganic course according to procedures by Carlucci *et al.* (2002) and Coe (2004). Crystals of the title compound were grown from a slow diffusion of hexanes into a solution of the ruthenium complex dissolved in dichloromethane.

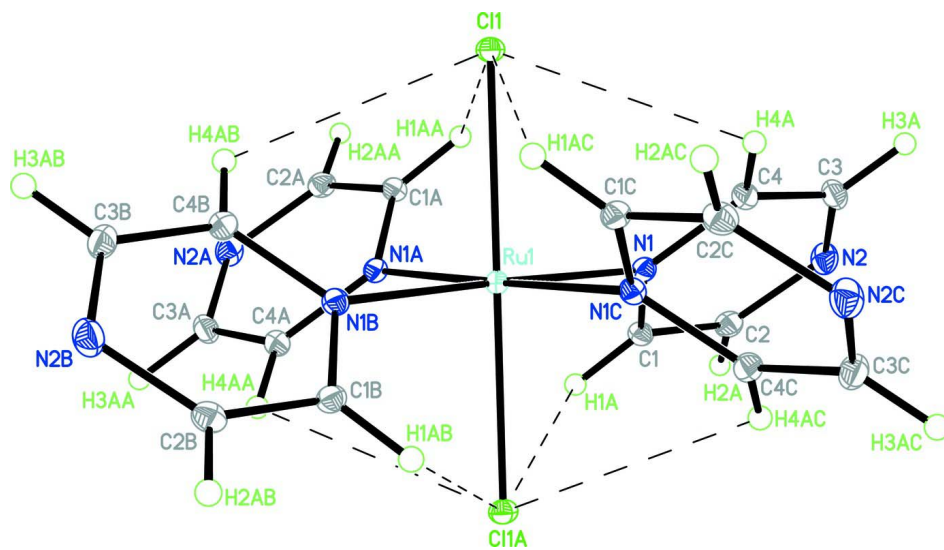
S3. Refinement

The H atoms attached to C atoms of the pyrazine molecules were placed in idealized positions (C—H = 0.95 Å) and allowed to ride on their parent atoms. Their positions were constrained so that the $U_{\text{iso}}(\text{H})$ was equal to $1.2U_{\text{eq}}$ of their respective parent atoms. The solvent molecule, CH_2Cl_2 , occupies a special position in the unit cell so the H atom was located using a difference map and was refined with a constrained $U_{\text{iso}}(\text{H})$ equal to $1.2U_{\text{eq}}$ of its parent atom.

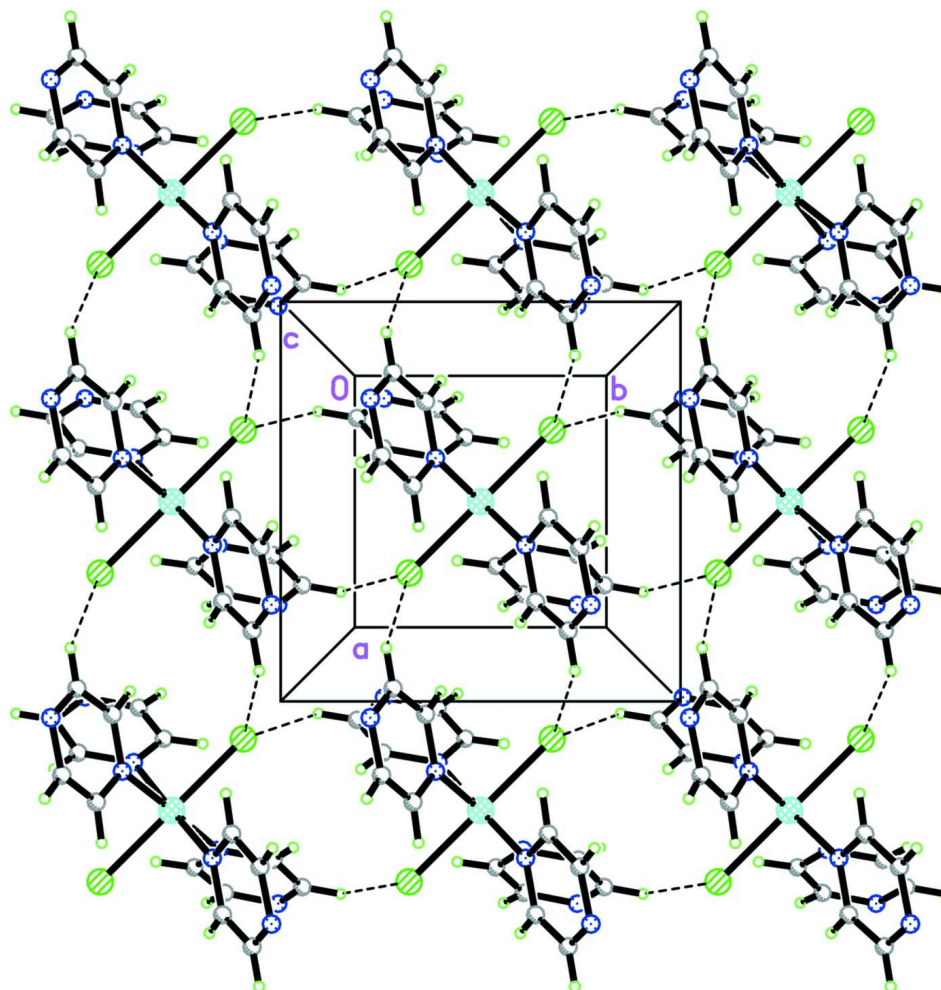
The maximum and minimum residual electron density peaks of 1.01 and 0.37 $\text{e}\text{\AA}^{-3}$, respectively, were located 1.44 Å and 0.76 Å from the H4A and Ru1 atoms, respectively, with the large residue most likely due to imperfect absorption corrections frequently encountered in heavy-metal atom structures.

**Figure 1**

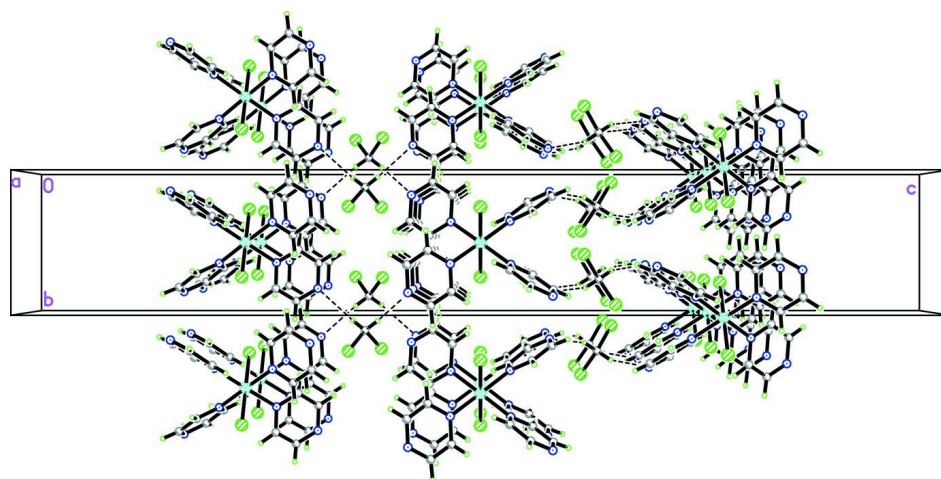
View of the title compound with 50% probability displacement ellipsoids.

**Figure 2**

View of the title compound showing intramolecular Cl...H contacts.

**Figure 3**

Fragment of the crystal packing of the compound along a *c* axis (dashed lines are Cl...H contacts).

**Figure 4**

Fragment of the crystal packing of the compound along an *a* axis (dashed lines are C—H...N H-bonds).

trans-Dichloridotetrapyrazineruthenium(II) dichloromethane disolvate

Crystal data

[RuCl₂(C₄H₄N₂)₄]₂·2CH₂Cl₂
M_r = 662.19
 Tetragonal, *I*₄22
 Hall symbol: I 4bw 2bw
a = 7.3059 (2) Å
c = 47.3659 (16) Å
V = 2528.21 (14) Å³
Z = 4
F(000) = 1320

D_x = 1.740 Mg m⁻³
 Mo *Kα* radiation, λ = 0.71073 Å
 Cell parameters from 8671 reflections
 θ = 2.8–27.0°
 μ = 1.28 mm⁻¹
T = 100 K
 Plate, black
 0.10 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 1996)
T_{min} = 0.882, *T_{max}* = 0.908

15409 measured reflections
 1399 independent reflections
 1363 reflections with *I* > 2σ(*I*)
R_{int} = 0.030
 θ_{max} = 27.0°, θ_{min} = 1.7°
h = -9→9
k = -9→9
l = -60→60

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.016
wR(*F*²) = 0.040
S = 1.03
 1399 reflections
 81 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/[σ²(*F_o*²) + (0.022*P*)² + 2.540*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 1.01 e Å⁻³
 Δρ_{min} = -0.38 e Å⁻³
 Absolute structure: Flack (1983), 508 Friedel
 pairs
 Absolute structure parameter: 0.26 (4)

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 > σ(*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)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
Ru1	1.0000	0.5000	0.2500	0.01016 (7)
Cl1	0.76849 (5)	0.26849 (5)	0.2500	0.01419 (11)
N1	0.8611 (2)	0.6437 (2)	0.21927 (3)	0.0125 (3)

C1	0.9492 (2)	0.7136 (2)	0.19664 (3)	0.0140 (3)
H1A	1.0775	0.6961	0.1949	0.017*
Cl2	0.74959 (8)	0.41921 (8)	0.141441 (10)	0.02798 (12)
N2	0.6770 (2)	0.8453 (2)	0.17735 (3)	0.0194 (3)
C2	0.8562 (2)	0.8101 (2)	0.17601 (4)	0.0163 (4)
H2A	0.9230	0.8534	0.1601	0.020*
C3	0.5910 (3)	0.7769 (3)	0.19991 (4)	0.0178 (4)
H3A	0.4634	0.7987	0.2019	0.021*
C4	0.6795 (3)	0.6757 (2)	0.22056 (3)	0.0146 (3)
H4A	0.6108	0.6279	0.2359	0.018*
C5	0.6136 (4)	0.2500	0.1250	0.0271 (6)
H5A	0.546 (3)	0.309 (3)	0.1112 (4)	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.00969 (8)	0.00969 (8)	0.01110 (12)	0.00041 (10)	0.000	0.000
Cl1	0.01315 (16)	0.01315 (16)	0.0163 (2)	-0.0024 (2)	-0.00218 (17)	0.00218 (17)
N1	0.0128 (8)	0.0111 (7)	0.0134 (6)	0.0000 (5)	0.0006 (6)	-0.0012 (6)
C1	0.0121 (8)	0.0141 (8)	0.0159 (8)	-0.0009 (6)	0.0015 (6)	-0.0008 (7)
Cl2	0.0296 (3)	0.0277 (3)	0.0266 (3)	-0.0024 (2)	-0.0107 (2)	-0.0016 (2)
N2	0.0207 (8)	0.0184 (8)	0.0191 (7)	0.0031 (6)	-0.0011 (7)	0.0044 (6)
C2	0.0187 (9)	0.0150 (9)	0.0153 (8)	-0.0017 (7)	0.0023 (7)	0.0015 (7)
C3	0.0133 (9)	0.0194 (9)	0.0207 (9)	0.0024 (7)	0.0013 (7)	0.0011 (7)
C4	0.0135 (9)	0.0147 (9)	0.0157 (7)	0.0000 (6)	0.0011 (7)	0.0005 (7)
C5	0.0182 (14)	0.0382 (19)	0.0249 (14)	0.000	0.000	-0.0117 (14)

Geometric parameters (Å, °)

Ru1—N1	2.0620 (14)	Cl2—C5	1.7668 (17)
Ru1—N1 ⁱ	2.0620 (14)	N2—C2	1.336 (2)
Ru1—N1 ⁱⁱ	2.0620 (14)	N2—C3	1.337 (2)
Ru1—N1 ⁱⁱⁱ	2.0620 (14)	C2—H2A	0.9500
Ru1—Cl1 ⁱⁱⁱ	2.3920 (5)	C3—C4	1.386 (3)
Ru1—Cl1	2.3920 (5)	C3—H3A	0.9500
N1—C4	1.349 (2)	C4—H4A	0.9500
N1—C1	1.351 (2)	C5—Cl2 ^{iv}	1.7668 (17)
C1—C2	1.383 (2)	C5—H5A	0.92 (2)
C1—H1A	0.9500		
N1—Ru1—N1 ⁱ	89.82 (8)	C1—N1—Ru1	121.20 (12)
N1—Ru1—N1 ⁱⁱ	178.62 (9)	N1—C1—C2	121.29 (16)
N1 ⁱ —Ru1—N1 ⁱⁱ	90.20 (7)	N1—C1—H1A	119.4
N1—Ru1—N1 ⁱⁱⁱ	90.20 (7)	C2—C1—H1A	119.4
N1 ⁱ —Ru1—N1 ⁱⁱⁱ	178.62 (9)	C2—N2—C3	115.27 (16)
N1 ⁱⁱ —Ru1—N1 ⁱⁱⁱ	89.82 (7)	N2—C2—C1	123.07 (17)
N1—Ru1—Cl1 ⁱⁱⁱ	89.31 (5)	N2—C2—H2A	118.5
N1 ⁱ —Ru1—Cl1 ⁱⁱⁱ	90.69 (5)	C1—C2—H2A	118.5

N1 ⁱⁱ —Ru1—Cl1 ⁱⁱⁱ	89.31 (5)	N2—C3—C4	122.98 (17)
N1 ⁱⁱⁱ —Ru1—Cl1 ⁱⁱⁱ	90.69 (5)	N2—C3—H3A	118.5
N1—Ru1—Cl1	90.69 (5)	C4—C3—H3A	118.5
N1 ⁱ —Ru1—Cl1	89.31 (5)	N1—C4—C3	121.27 (16)
N1 ⁱⁱ —Ru1—Cl1	90.69 (5)	N1—C4—H4A	119.4
N1 ⁱⁱⁱ —Ru1—Cl1	89.31 (5)	C3—C4—H4A	119.4
Cl1 ⁱⁱⁱ —Ru1—Cl1	180.0	Cl2—C5—Cl2 ^{iv}	111.58 (16)
C4—N1—C1	116.08 (15)	Cl2—C5—H5A	106.7 (15)
C4—N1—Ru1	122.71 (12)	Cl2 ^{iv} —C5—H5A	108.1 (15)

Symmetry codes: (i) $-y+3/2, -x+3/2, -z+1/2$; (ii) $y+1/2, x-1/2, -z+1/2$; (iii) $-x+2, -y+1, z$; (iv) $x, -y+1/2, -z+1/4$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C3—H3A \cdots Cl1 ^v	0.95	2.88	3.555 (2)	129
C5—H5A \cdots N2 ^{vi}	0.92 (2)	2.46 (2)	3.338 (2)	158 (2)

Symmetry codes: (v) $-x+1, -y+1, z$; (vi) $-x+1, y-1/2, -z+1/4$.