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[2,6-Bis(5-chloropyrimidin-2-yl-κN)-pyridine-κN](2,2′:6′,2″-terpyridine-$\kappa^3 N,N',N''$)ruthenium(II) bis(hexafluoridophosphate) acetonitrile disolvate

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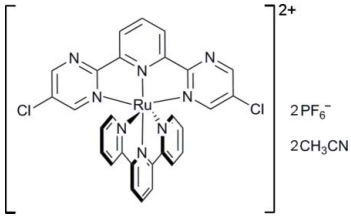
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.029; wR factor = 0.073; data-to-parameter ratio = 13.7.

In the title compound, $[Ru(C_{13}H_7Cl_2N_5)(C_{15}H_{11}N_3)](PF_6)_2\cdot 2CH_3CN$, the Ru^{II} atom is coordinated in a distorted octahedral geometry by a tridentate 2,2′:6′,2″-terpyridine ligand and a tridentate 2,6-bis(5-chloropyrimidin-2-yl)pyridine ligand. Least-squares mean-plane distortions of only 1.72 (2) and 2.91 (2)° of the pyrimidyl rings with respect to the central pyridine are observed for the bis(pyrimidyl)pyridine-based tridentate ligand, while the distal pyridyl rings of terpyridine twist by 13.43 (7) and 4.68 (9)° away from the central pyridine ring.

Related literature

For related literature, see: Fang *et al.* (2002); Groen *et al.* (1998); Medlycott & Hanan (2005); Polson *et al.* (2004); Pyo *et al.* (1999).



Experimental

Crystal data

$[Ru(C_{13}H_7Cl_2N_5)(C_{15}H_{11}N_3)](PF_6)_2\cdot 2C_2H_3N$
M_r = 1010.52
Orthorhombic, $Fdd2$
a = 16.3846 (2) Å
b = 62.8985 (8) Å
c = 14.5581 (2) Å
V = 15003.1 (3) Å^3
Z = 16
Cu $K\alpha$ radiation
μ = 6.43 mm^{-1}
T = 100 (2) K
0.48 × 0.25 × 0.07 mm

Data collection

Bruker SMART 2K diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.190, T_{max} = 0.640
45518 measured reflections
7327 independent reflections
7121 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.072
S = 1.08
7327 reflections
534 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Absolute structure: Flack (1983), 3439 Friedel pairs
Flack parameter: 0.052 (5)

Table 1
Selected geometric parameters (Å, °).

Ru1—N1	2.088 (2)	Ru1—N6	2.083 (3)
Ru1—N3	1.980 (2)	Ru1—N7	2.000 (2)
Ru1—N4	2.069 (2)	Ru1—N8	2.068 (3)
N3—Ru1—N7	175.35 (9)	N8—Ru1—N6	157.58 (9)
N3—Ru1—N8	100.81 (12)	N4—Ru1—N6	91.4 (1)
N7—Ru1—N8	78.90 (12)	N3—Ru1—N1	79.51 (9)
N3—Ru1—N4	79.37 (9)	N7—Ru1—N1	105.12 (9)
N7—Ru1—N4	96.00 (9)	N8—Ru1—N1	90.79 (10)
N8—Ru1—N4	92.69 (10)	N4—Ru1—N1	158.87 (9)
N3—Ru1—N6	101.62 (11)	N6—Ru1—N1	93.3 (1)
N7—Ru1—N6	78.75 (11)		

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX* (local program) and Spek (2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2110).

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supplementary materials

Acta Cryst. (2008). E**64**, m326 [**doi:10.1107/S1600536807068602**]

[2,6-Bis(5-chloropyrimidin-2-yl-κN)pyridine-κN](2,2':6',2''-terpyridine-$\kappa^3 N,N',N''$)ruthenium(II) bis(hexafluoridophosphate) acetonitrile disolvate

E. A. Medlycott, J. Wang and G. S. Hanan

Comment

Ruthenium(II) complexes of tridentate polypyridine ligands have gained much attention in the last few decades due to their interesting photophysical properties. There have been many attempts to try and improve the photophysical properties of these complexes both in the ground state and excited states (Medlycott & Hanan, 2005). Manipulation of the electronic properties of the coordinated ligands can result in an improvement of the photophysical properties of the complex. We have previously employed this strategy by using electron-deficient trazine-based tridenate ligands (Polson *et al.*, 2004) to lower the energy of the ^{3}MLCT emitting state. Herein, we employ a functionalized bis(pyrimidin-2-yl)pyridine tridentate ligand for the synthesis of a ruthenium(II) complex in order to manipulate the energy of the ^{3}MLCT emitting state. A structurally similar ligand, namely bis(pyrimidin-2-yl)pyridine, has previously been employed for the synthesis of palladium(II) complexes in order to study the dynamic behviour of such complexes in solution (Groen *et al.*, 1998). However, the electronic behaviour and solid state structures of these systems were not reported.

The title compound crystalizes in the orthorhombic space group *Fdd*2 with one complex cation, two PF_6^- anions and two acetonitrile molecules in the asymmetric unit. The complex possesses octahedral geometry with significant distortions due to the tridentate nature of the coordinating ligands as previously observed in the parent complex $[Ru(tpy)_2]^{2+}$ (tpy = 2,2':6',2"-terpyridine) (Pyo *et al.*, 1999). Small variations in the Ru—N bond distances are observed between the two coordinated ligands indicating minimal changes in the electronic (solid state) ground-state properties of the complex compared to $[Ru(tpy)_2]^{2+}$ (Pyo *et al.*, 1999). Similarly, small changes are observed in the *N,N,N*-tridentate bite angles on the pyrimidyl-substituted ligand 158.87 (9)° compared to the coordinated tpy, 157.58 (9)°, indicating that introducing a pyrimidyl ring has minimal steric effects on the ligand field of the complex.

Comparison of the planarity of the two coordinated ligands in the title compound shows us that the bis(pyrimidin-2-yl)pyridine-based ligand lies planar. Least-square mean plane distortions of only 1.72 (2)° and 2.91 (2)° of the pyrimidyl rings with respect to the central pyridine are observed. However, the distal pyridyl-rings of terpyridine twist by 13.43 (7)° and 4.68 (9)° away from the central pyridine ring. This difference may be explained on considering the uncoordinated pyrimidyl-N atoms forming favourable intramolecular C–H···N interactions with the central pyridine ring. This coplanar effect has previously been shown to dramatically enhance the photophysical properties of such complexes (Fang *et al.*, 2002).

We are currently investigating the consequences of pyrimidyl substitution of tridentate-tpy based ligands on the photophysical properties of their ruthenium(II) complexes.

Experimental

The title compound was synthesized following previously established procedures (Polson *et al.*,2004).

Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.95Å and U_{iso}(H) = 1.2U_{eq}(C) for the ligands and with C—H = 0.98Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl group of acetonitrile. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 2003).

Figures

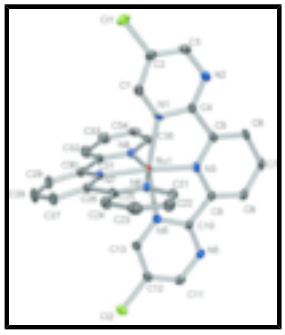


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. The PF_6^- counter anions, H atoms and acetonitrile solvent molecules have been omitted for clarity.

[2,6-Bis(5-chloropyrimidin-2-yl)pyridine-κ^3*N*^{1},*N*^{2},*N*^{6}](2,2':6',2''- terpyridine-κ^3*N*,*N*',*N*'')ruthenium(II) bis(hexafluoridophosphate) acetonitrile disolvate

Crystal data

$[Ru(C_{13}H_7Cl_2N_5)(C_{15}H_{11}N_3)](PF_6)_2{\cdot}2C_2H_3N$	F_{000} = 8032
M_r = 1010.52	D_x = 1.789 Mg m^{-3}
Orthorhombic, *Fdd*2	Cu *K*α radiation λ = 1.54178 Å
Hall symbol: F 2 -2d	Cell parameters from 7885 reflections
a = 16.3846 (2) Å	θ = 2.8–72.9º
b = 62.8985 (8) Å	μ = 6.44 mm^{-1}
c = 14.5581 (2) Å	*T* = 100 (2) K
V = 15003.1 (3) Å^3	Block, red
Z = 16	0.48 × 0.25 × 0.07 mm

Data collection

Bruker SMART 2K diffractometer	7327 independent reflections
Radiation source: X-ray Sealed Tube	7121 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.053
T = 100(2) K	θ_{max} = 73.0º
ω scans	θ_{min} = 2.8º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	*h* = −19→18
T_{min} = 0.190, T_{max} = 0.640	*k* = −77→77

45518 measured reflections

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.072$

$S = 1.08$

7327 reflections

534 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.71$ e Å^{-3}

$\Delta\rho_{min} = -0.38$ e Å^{-3}

Extinction correction: none

Absolute structure: Flack (1983), 3439 Friedel pairs

Flack parameter: 0.052 (5)

Special details

Experimental. X-ray crystallographic data for the title compound were collected from a single-crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker *SMART* 2 K Charged-Coupled Device (CCD) Area Detector using the program *SMART* and normal focus sealed tube source graphite monochromated Cu—Kα radiation. The crystal-to-detector distance was 4.908 cm, and the data collection was carried out in 512 *x* 512 pixel mode, utilizing 4 *x* 4 pixel binning. The initial unit-cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 9.0 degree scan in 30 frames over four different parts of the reciprocal space (120 frames total). One complete sphere of data was collected, to better than 0.8Å resolution. Upon completion of the data collection, the first 101 frames were recollected in order to improve the decay correction analysis.

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.290100 (12)	0.172144 (3)	0.184589 (14)	0.01338 (6)
N1	0.16426 (13)	0.16743 (3)	0.17514 (17)	0.0127 (5)
N2	0.06878 (15)	0.13822 (4)	0.16488 (17)	0.0192 (5)
N3	0.28547 (14)	0.14071 (3)	0.1797 (2)	0.0158 (4)
N4	0.41289 (14)	0.16477 (4)	0.19327 (18)	0.0162 (5)
N5	0.50172 (15)	0.13428 (4)	0.19511 (18)	0.0185 (5)
N6	0.30146 (14)	0.17985 (4)	0.04606 (19)	0.0161 (5)
N7	0.30453 (13)	0.20369 (3)	0.1912 (2)	0.0171 (5)
N8	0.28073 (15)	0.17725 (4)	0.32451 (18)	0.0164 (5)
Cl1	−0.05599 (5)	0.191627 (12)	0.18178 (7)	0.03047 (17)
Cl2	0.63956 (5)	0.185785 (12)	0.20297 (6)	0.02663 (17)
C1	0.10321 (18)	0.18085 (4)	0.1752 (2)	0.0187 (6)

H1	0.1139	0.1957	0.1764	0.022*
C2	0.02315 (19)	0.17372 (5)	0.1736 (2)	0.0216 (6)
C3	0.00786 (18)	0.15218 (5)	0.1673 (2)	0.0205 (6)
H3	−0.0469	0.1473	0.1648	0.025*
C4	0.14379 (17)	0.14580 (4)	0.1707 (2)	0.0161 (6)
C5	0.21284 (17)	0.13084 (4)	0.1747 (2)	0.0166 (6)
C6	0.20777 (17)	0.10876 (4)	0.1748 (2)	0.0179 (6)
H6	0.1563	0.1018	0.1723	0.021*
C7	0.27997 (18)	0.09704 (4)	0.1786 (2)	0.0195 (6)
H7	0.2782	0.0819	0.1792	0.023*
C8	0.35412 (17)	0.10751 (4)	0.1814 (2)	0.0184 (5)
H8	0.4036	0.0996	0.1816	0.022*
C9	0.35616 (16)	0.12949 (4)	0.1840 (2)	0.0157 (5)
C10	0.42780 (17)	0.14324 (4)	0.1912 (2)	0.0155 (5)
C11	0.56623 (19)	0.14731 (5)	0.1980 (2)	0.0194 (6)
H11	0.6197	0.1415	0.1991	0.023*
C12	0.55631 (19)	0.16922 (5)	0.1993 (2)	0.0195 (6)
C13	0.47850 (17)	0.17753 (5)	0.1987 (2)	0.0175 (6)
H13	0.4711	0.1925	0.2022	0.021*
C21	0.30071 (18)	0.16651 (5)	−0.0258 (2)	0.0195 (6)
H21	0.2985	0.1516	−0.0147	0.023*
C22	0.3031 (2)	0.17365 (5)	−0.1157 (2)	0.0246 (7)
H22	0.3032	0.1638	−0.1651	0.029*
C23	0.3053 (2)	0.19512 (6)	−0.1327 (2)	0.0264 (7)
H23	0.3035	0.2003	−0.1939	0.032*
C24	0.31023 (19)	0.20912 (5)	−0.0588 (3)	0.0236 (6)
H24	0.3144	0.2240	−0.0690	0.028*
C25	0.30901 (18)	0.20109 (5)	0.0297 (2)	0.0176 (6)
C26	0.31643 (18)	0.21439 (5)	0.1127 (2)	0.0181 (6)
C27	0.3406 (2)	0.23558 (5)	0.1156 (2)	0.0229 (7)
H27	0.3490	0.2434	0.0606	0.028*
C28	0.3523 (2)	0.24505 (5)	0.2008 (2)	0.0283 (7)
H28	0.3690	0.2595	0.2040	0.034*
C29	0.3398 (2)	0.23369 (5)	0.2810 (2)	0.0246 (7)
H29	0.3481	0.2402	0.3392	0.030*
C30	0.31470 (19)	0.21252 (5)	0.2749 (2)	0.0193 (6)
C31	0.29853 (18)	0.19766 (5)	0.3507 (2)	0.0191 (6)
C32	0.3001 (2)	0.20342 (5)	0.4418 (3)	0.0257 (7)
H32	0.3149	0.2175	0.4591	0.031*
C33	0.2797 (2)	0.18839 (6)	0.5089 (2)	0.0262 (7)
H33	0.2806	0.1922	0.5721	0.031*
C34	0.25841 (19)	0.16815 (6)	0.4826 (2)	0.0241 (7)
H34	0.2430	0.1578	0.5270	0.029*
C35	0.25996 (19)	0.16315 (5)	0.3895 (2)	0.0202 (6)
H35	0.2457	0.1491	0.3712	0.024*
P1	0.53369 (4)	0.138455 (11)	−0.06986 (7)	0.01995 (15)
F11	0.55805 (15)	0.15979 (3)	−0.12300 (15)	0.0394 (5)
F12	0.47251 (14)	0.15156 (4)	−0.00468 (16)	0.0489 (6)
F13	0.60507 (12)	0.14221 (4)	0.00174 (15)	0.0395 (5)

F14	0.59497 (16)	0.12565 (4)	−0.13491 (16)	0.0478 (6)
F15	0.46190 (13)	0.13468 (4)	−0.14174 (17)	0.0456 (6)
F16	0.50911 (17)	0.11725 (4)	−0.01669 (18)	0.0514 (7)
P2	0.55212 (6)	0.220273 (12)	0.44248 (8)	0.02989 (19)
F21	0.62202 (18)	0.23668 (4)	0.41314 (18)	0.0620 (8)
F22	0.61423 (13)	0.20103 (4)	0.4277 (2)	0.0494 (6)
F23	0.52253 (16)	0.21836 (4)	0.33806 (17)	0.0481 (6)
F24	0.4896 (2)	0.23943 (4)	0.45789 (19)	0.0691 (9)
F25	0.57961 (18)	0.22231 (4)	0.54775 (16)	0.0499 (6)
F26	0.48287 (14)	0.20363 (4)	0.47239 (17)	0.0412 (5)
C41	0.5921 (3)	0.24842 (7)	0.1749 (4)	0.0671 (15)
H41A	0.5672	0.2485	0.2362	0.101*
H41B	0.6125	0.2341	0.1613	0.101*
H41C	0.5511	0.2524	0.1291	0.101*
C42	0.6591 (3)	0.26342 (6)	0.1723 (3)	0.0385 (9)
N43	0.7112 (2)	0.27540 (5)	0.1708 (3)	0.0412 (9)
C51	0.5307 (3)	0.20455 (7)	−0.0195 (3)	0.0445 (10)
H51A	0.5680	0.2005	0.0302	0.067*
H51B	0.4951	0.1925	−0.0341	0.067*
H51C	0.4974	0.2167	0.0000	0.067*
C52	0.5776 (2)	0.21037 (5)	−0.1004 (3)	0.0301 (8)
N53	0.6152 (2)	0.21498 (5)	−0.1637 (2)	0.0403 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ru1	0.01374 (10)	0.00810 (9)	0.01831 (10)	0.00004 (7)	0.00117 (8)	0.00034 (9)
N1	0.0076 (10)	0.0176 (11)	0.0129 (12)	−0.0043 (8)	−0.0006 (9)	0.0052 (10)
N2	0.0179 (13)	0.0198 (12)	0.0198 (14)	−0.0043 (10)	−0.0001 (10)	0.0000 (10)
N3	0.0191 (11)	0.0120 (10)	0.0164 (11)	0.0004 (8)	−0.0004 (10)	0.0014 (12)
N4	0.0171 (12)	0.0150 (11)	0.0167 (12)	−0.0012 (8)	0.0020 (11)	−0.0005 (11)
N5	0.0189 (12)	0.0146 (11)	0.0220 (13)	0.0035 (8)	0.0033 (11)	0.0011 (10)
N6	0.0139 (12)	0.0110 (12)	0.0233 (14)	−0.0003 (9)	0.0007 (10)	0.0012 (10)
N7	0.0165 (12)	0.0104 (10)	0.0243 (13)	0.0007 (8)	0.0028 (12)	0.0009 (11)
N8	0.0151 (12)	0.0151 (12)	0.0191 (13)	−0.0002 (9)	−0.0001 (9)	−0.0003 (10)
Cl1	0.0194 (3)	0.0265 (4)	0.0456 (5)	0.0084 (3)	0.0040 (4)	0.0037 (4)
Cl2	0.0186 (4)	0.0253 (4)	0.0360 (5)	−0.0046 (3)	0.0018 (3)	−0.0041 (3)
C1	0.0202 (14)	0.0153 (12)	0.0205 (15)	−0.0006 (10)	0.0014 (13)	0.0026 (11)
C2	0.0188 (13)	0.0230 (14)	0.0230 (18)	0.0043 (11)	0.0024 (13)	0.0019 (13)
C3	0.0134 (14)	0.0280 (15)	0.0200 (16)	−0.0011 (11)	−0.0002 (11)	−0.0008 (12)
C4	0.0182 (14)	0.0148 (12)	0.0153 (15)	−0.0016 (10)	0.0032 (11)	−0.0023 (11)
C5	0.0199 (13)	0.0148 (12)	0.0150 (15)	−0.0041 (10)	0.0014 (11)	0.0004 (12)
C6	0.0207 (13)	0.0128 (12)	0.0202 (16)	−0.0050 (10)	0.0020 (12)	−0.0008 (12)
C7	0.0275 (15)	0.0089 (11)	0.0220 (15)	0.0012 (10)	0.0001 (13)	0.0009 (13)
C8	0.0240 (14)	0.0129 (12)	0.0183 (13)	0.0039 (10)	0.0012 (14)	0.0025 (12)
C9	0.0181 (13)	0.0120 (12)	0.0171 (13)	0.0008 (9)	0.0015 (13)	0.0015 (12)
C10	0.0179 (13)	0.0139 (12)	0.0146 (13)	0.0043 (9)	0.0001 (12)	0.0011 (12)
C11	0.0167 (14)	0.0236 (14)	0.0178 (15)	0.0030 (11)	0.0007 (12)	0.0019 (12)

C12	0.0185 (14)	0.0202 (14)	0.0197 (18)	−0.0038 (11)	0.0021 (12)	−0.0029 (12)
C13	0.0176 (14)	0.0164 (13)	0.0184 (15)	−0.0020 (10)	0.0035 (12)	−0.0011 (11)
C21	0.0166 (15)	0.0147 (14)	0.0272 (16)	−0.0008 (11)	−0.0005 (12)	−0.0031 (12)
C22	0.0254 (17)	0.0258 (17)	0.0225 (17)	−0.0011 (13)	0.0016 (13)	−0.0064 (13)
C23	0.0259 (17)	0.0316 (19)	0.0218 (16)	−0.0009 (14)	0.0022 (13)	0.0042 (14)
C24	0.0235 (15)	0.0196 (14)	0.0277 (17)	−0.0016 (11)	0.0048 (15)	0.0047 (14)
C25	0.0160 (14)	0.0130 (14)	0.0237 (15)	−0.0031 (11)	0.0010 (12)	0.0025 (12)
C26	0.0148 (14)	0.0148 (14)	0.0247 (16)	0.0009 (11)	0.0005 (12)	0.0013 (12)
C27	0.0269 (16)	0.0126 (14)	0.0293 (17)	−0.0019 (12)	0.0033 (13)	0.0021 (12)
C28	0.0359 (19)	0.0136 (14)	0.035 (2)	−0.0055 (12)	0.0036 (15)	−0.0036 (13)
C29	0.0305 (17)	0.0147 (14)	0.0287 (17)	−0.0020 (12)	0.0007 (14)	−0.0057 (12)
C30	0.0168 (15)	0.0174 (15)	0.0237 (16)	0.0009 (11)	0.0008 (12)	−0.0040 (12)
C31	0.0157 (15)	0.0159 (15)	0.0258 (17)	0.0005 (11)	0.0024 (12)	−0.0006 (12)
C32	0.0273 (16)	0.0277 (17)	0.0222 (16)	−0.0046 (12)	−0.0017 (14)	−0.0065 (15)
C33	0.0233 (17)	0.034 (2)	0.0213 (16)	−0.0021 (14)	0.0001 (13)	−0.0002 (14)
C34	0.0149 (16)	0.0327 (18)	0.0245 (16)	−0.0007 (13)	−0.0002 (13)	0.0058 (14)
C35	0.0159 (15)	0.0171 (14)	0.0277 (16)	−0.0009 (11)	0.0008 (12)	0.0045 (12)
P1	0.0173 (3)	0.0206 (3)	0.0220 (4)	−0.0014 (3)	−0.0014 (3)	0.0043 (4)
F11	0.0604 (15)	0.0288 (11)	0.0290 (11)	−0.0096 (10)	−0.0010 (10)	0.0081 (9)
F12	0.0412 (13)	0.0762 (18)	0.0295 (12)	0.0268 (12)	0.0053 (10)	0.0076 (12)
F13	0.0272 (11)	0.0636 (15)	0.0277 (11)	−0.0158 (10)	−0.0083 (9)	0.0098 (10)
F14	0.0543 (15)	0.0551 (15)	0.0339 (12)	0.0287 (12)	0.0038 (11)	0.0004 (11)
F15	0.0329 (13)	0.0671 (17)	0.0369 (13)	−0.0200 (11)	−0.0104 (10)	0.0106 (12)
F16	0.0697 (17)	0.0369 (13)	0.0477 (15)	−0.0190 (12)	−0.0112 (13)	0.0209 (11)
P2	0.0418 (5)	0.0167 (3)	0.0312 (5)	−0.0054 (3)	0.0004 (4)	−0.0044 (4)
F21	0.093 (2)	0.0467 (14)	0.0464 (16)	−0.0465 (14)	−0.0020 (14)	0.0039 (12)
F22	0.0305 (11)	0.0396 (12)	0.0783 (18)	−0.0016 (9)	0.0024 (13)	−0.0136 (14)
F23	0.0615 (16)	0.0487 (15)	0.0342 (12)	−0.0094 (12)	−0.0039 (11)	−0.0094 (11)
F24	0.116 (3)	0.0338 (13)	0.0576 (19)	0.0370 (15)	0.0013 (16)	−0.0069 (12)
F25	0.0831 (19)	0.0298 (12)	0.0367 (13)	−0.0235 (12)	−0.0118 (12)	0.0036 (10)
F26	0.0352 (12)	0.0343 (12)	0.0541 (14)	−0.0045 (9)	0.0122 (10)	−0.0061 (10)
C41	0.074 (3)	0.048 (3)	0.080 (4)	−0.016 (2)	−0.032 (3)	0.020 (3)
C42	0.054 (2)	0.0251 (17)	0.036 (2)	0.0097 (16)	−0.0056 (19)	0.0037 (16)
N43	0.050 (2)	0.0265 (15)	0.047 (2)	0.0066 (14)	0.0009 (16)	0.0026 (15)
C51	0.044 (2)	0.044 (2)	0.045 (2)	−0.0034 (18)	0.0125 (19)	0.0020 (19)
C52	0.0322 (19)	0.0219 (16)	0.036 (2)	0.0064 (13)	−0.0042 (15)	−0.0004 (14)
N53	0.053 (2)	0.0313 (17)	0.0368 (18)	0.0028 (14)	0.0104 (16)	0.0072 (14)

Geometric parameters (Å, °)

Ru1—N1	2.088 (2)	C22—H22	0.95
Ru1—N3	1.980 (2)	C23—C24	1.393 (5)
Ru1—N4	2.069 (2)	C23—H23	0.95
Ru1—N6	2.083 (3)	C24—C25	1.383 (5)
Ru1—N7	2.000 (2)	C24—H24	0.95
Ru1—N8	2.068 (3)	C25—C26	1.475 (4)
N1—C1	1.309 (4)	C26—C27	1.391 (4)
N1—C4	1.403 (3)	C27—C28	1.389 (5)
N2—C4	1.321 (4)	C27—H27	0.95

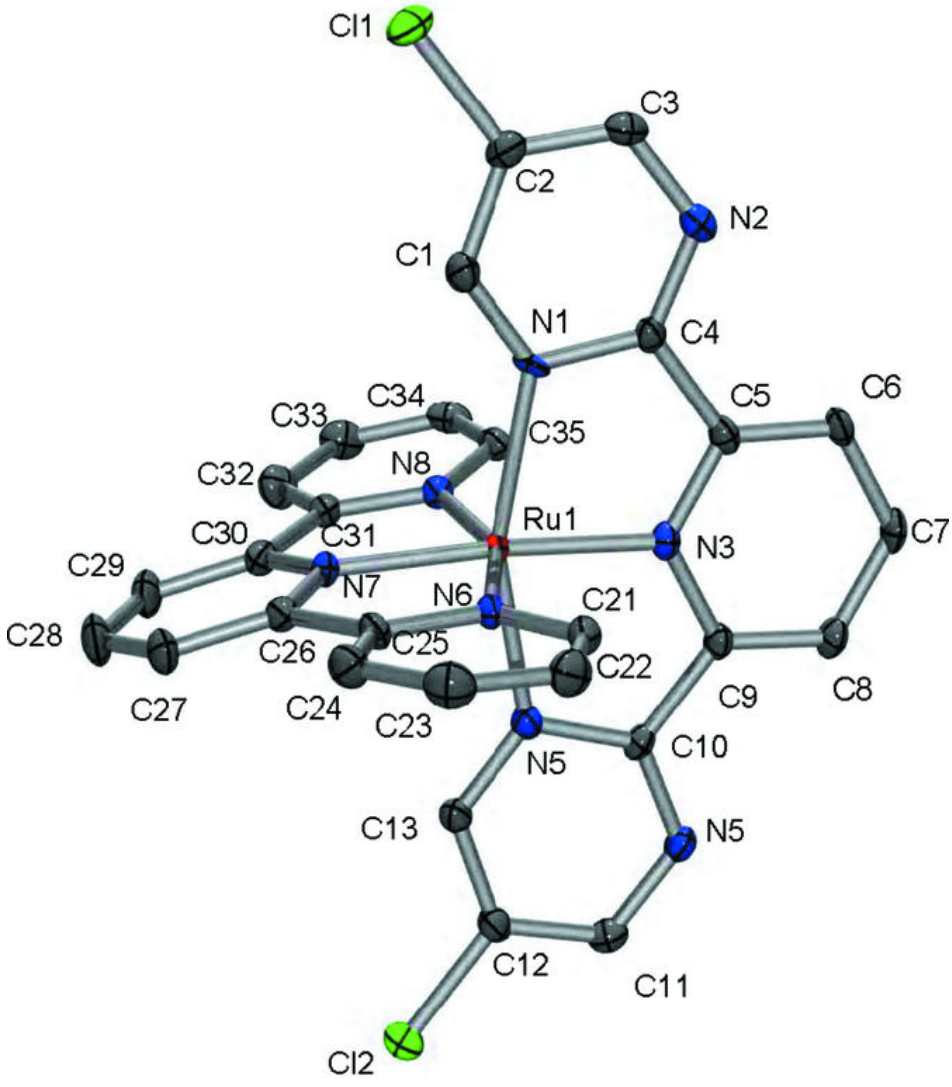
N2—C3	1.330 (4)	C28—C29	1.384 (5)
N3—C5	1.344 (4)	C28—H28	0.95
N3—C9	1.358 (3)	C29—C30	1.396 (4)
N4—C13	1.344 (4)	C29—H29	0.95
N4—C10	1.376 (3)	C30—C31	1.471 (4)
N5—C10	1.337 (3)	C31—C32	1.375 (5)
N5—C11	1.339 (4)	C32—C33	1.399 (5)
N6—C21	1.342 (4)	C32—H32	0.95
N6—C25	1.363 (4)	C33—C34	1.375 (5)
N7—C26	1.340 (4)	C33—H33	0.95
N7—C30	1.349 (4)	C34—C35	1.392 (4)
N8—C35	1.341 (4)	C34—H34	0.95
N8—C31	1.370 (4)	C35—H35	0.95
Cl1—C2	1.722 (3)	P1—F13	1.584 (2)
Cl2—C12	1.717 (3)	P1—F15	1.592 (2)
C1—C2	1.386 (4)	P1—F16	1.594 (2)
C1—H1	0.95	P1—F14	1.598 (2)
C2—C3	1.381 (4)	P1—F11	1.599 (2)
C3—H3	0.95	P1—F12	1.608 (2)
C4—C5	1.473 (4)	P2—F22	1.596 (2)
C5—C6	1.391 (4)	P2—F24	1.598 (3)
C6—C7	1.395 (4)	P2—F21	1.600 (2)
C6—H6	0.95	P2—F23	1.600 (3)
C7—C8	1.382 (4)	P2—F25	1.602 (2)
C7—H7	0.95	P2—F26	1.604 (2)
C8—C9	1.383 (4)	C41—C42	1.448 (6)
C8—H8	0.95	C41—H41a	0.98
C9—C10	1.462 (4)	C41—H41b	0.98
C11—C12	1.387 (4)	C41—H41c	0.98
C11—H11	0.95	C42—N43	1.140 (5)
C12—C13	1.378 (4)	C51—C52	1.453 (5)
C13—H13	0.95	C51—H51a	0.98
C21—C22	1.383 (5)	C51—H51b	0.98
C21—H21	0.95	C51—H51c	0.98
C22—C23	1.374 (5)	C52—N53	1.145 (5)
N3—Ru1—N7	175.35 (9)	C24—C23—H23	120.5
N3—Ru1—N8	100.81 (12)	C25—C24—C23	119.2 (3)
N7—Ru1—N8	78.90 (12)	C25—C24—H24	120.4
N3—Ru1—N4	79.37 (9)	C23—C24—H24	120.4
N7—Ru1—N4	96.00 (9)	N6—C25—C24	121.5 (3)
N8—Ru1—N4	92.69 (10)	N6—C25—C26	114.8 (3)
N3—Ru1—N6	101.62 (11)	C24—C25—C26	123.7 (3)
N7—Ru1—N6	78.75 (11)	N7—C26—C27	119.8 (3)
N8—Ru1—N6	157.58 (9)	N7—C26—C25	113.7 (3)
N4—Ru1—N6	91.4 (1)	C27—C26—C25	126.3 (3)
N3—Ru1—N1	79.51 (9)	C28—C27—C26	118.5 (3)
N7—Ru1—N1	105.12 (9)	C28—C27—H27	120.7
N8—Ru1—N1	90.79 (10)	C26—C27—H27	120.7
N4—Ru1—N1	158.87 (9)	C29—C28—C27	120.7 (3)

N6—Ru1—N1	93.3 (1)	C29—C28—H28	119.6
C1—N1—C4	116.3 (2)	C27—C28—H28	119.6
C1—N1—RU1	131.55 (19)	C28—C29—C30	118.8 (3)
C4—N1—RU1	112.15 (18)	C28—C29—H29	120.6
C4—N2—C3	117.3 (3)	C30—C29—H29	120.6
C5—N3—C9	121.2 (2)	N7—C30—C29	119.1 (3)
C5—N3—RU1	119.80 (18)	N7—C30—C31	113.2 (3)
C9—N3—RU1	119.00 (18)	C29—C30—C31	127.7 (3)
C13—N4—C10	116.5 (2)	N8—C31—C32	121.3 (3)
C13—N4—RU1	130.4 (2)	N8—C31—C30	115.1 (3)
C10—N4—RU1	113.08 (18)	C32—C31—C30	123.6 (3)
C10—N5—C11	117.3 (2)	C31—C32—C33	119.4 (3)
C21—N6—C25	118.5 (3)	C31—C32—H32	120.3
C21—N6—RU1	127.5 (2)	C33—C32—H32	120.3
C25—N6—RU1	113.9 (2)	C34—C33—C32	119.5 (3)
C26—N7—C30	123.0 (2)	C34—C33—H33	120.3
C26—N7—RU1	118.3 (2)	C32—C33—H33	120.3
C30—N7—RU1	117.8 (2)	C33—C34—C35	118.4 (3)
C35—N8—C31	118.5 (3)	C33—C34—H34	120.8
C35—N8—RU1	127.7 (2)	C35—C34—H34	120.8
C31—N8—RU1	113.8 (2)	N8—C35—C34	122.9 (3)
N1—C1—C2	121.0 (3)	N8—C35—H35	118.6
N1—C1—H1	119.5	C34—C35—H35	118.6
C2—C1—H1	119.5	F13—P1—F15	179.9 (2)
C3—C2—C1	119.3 (3)	F13—P1—F16	89.53 (13)
C3—C2—CL1	120.6 (2)	F15—P1—F16	90.45 (13)
C1—C2—CL1	120.0 (2)	F13—P1—F14	90.07 (13)
N2—C3—C2	120.9 (3)	F15—P1—F14	89.98 (15)
N2—C3—H3	119.6	F16—P1—F14	91.42 (15)
C2—C3—H3	119.6	F13—P1—F11	90.51 (12)
N2—C4—N1	125.1 (3)	F15—P1—F11	89.51 (13)
N2—C4—C5	119.1 (3)	F16—P1—F11	179.77 (18)
N1—C4—C5	115.7 (2)	F14—P1—F11	88.81 (14)
N3—C5—C6	120.9 (3)	F13—P1—F12	89.74 (14)
N3—C5—C4	112.8 (2)	F15—P1—F12	90.21 (13)
C6—C5—C4	126.3 (3)	F16—P1—F12	89.14 (15)
C5—C6—C7	118.5 (3)	F14—P1—F12	179.41 (16)
C5—C6—H6	120.8	F11—P1—F12	90.63 (14)
C7—C6—H6	120.8	F22—P2—F24	179.57 (19)
C8—C7—C6	119.7 (2)	F22—P2—F21	89.79 (15)
C8—C7—H7	120.2	F24—P2—F21	90.59 (18)
C6—C7—H7	120.2	F22—P2—F23	90.44 (15)
C7—C8—C9	119.9 (3)	F24—P2—F23	89.76 (15)
C7—C8—H8	120.1	F21—P2—F23	90.67 (14)
C9—C8—H8	120.1	F22—P2—F25	90.61 (16)
N3—C9—C8	119.8 (2)	F24—P2—F25	89.19 (15)
N3—C9—C10	112.4 (2)	F21—P2—F25	90.15 (13)
C8—C9—C10	127.8 (2)	F23—P2—F25	178.67 (18)
N5—C10—N4	125.1 (3)	F22—P2—F26	89.60 (12)

N5—C10—C9	118.7 (2)	F24—P2—F26	90.02 (16)
N4—C10—C9	116.2 (2)	F21—P2—F26	179.30 (17)
N5—C11—C12	121.1 (3)	F23—P2—F26	89.68 (13)
N5—C11—H11	119.5	F25—P2—F26	89.51 (14)
C12—C11—H11	119.5	C42—C41—H41A	109.5
C13—C12—C11	119.0 (3)	C42—C41—H41B	109.5
C13—C12—CL2	120.3 (2)	H41A—C41—H41B	109.5
C11—C12—CL2	120.7 (2)	C42—C41—H41C	109.5
N4—C13—C12	120.9 (3)	H41A—C41—H41C	109.5
N4—C13—H13	119.5	H41B—C41—H41C	109.5
C12—C13—H13	119.5	N43—C42—C41	179.1 (5)
N6—C21—C22	122.3 (3)	C52—C51—H51A	109.5
N6—C21—H21	118.9	C52—C51—H51B	109.5
C22—C21—H21	118.9	H51A—C51—H51B	109.5
C23—C22—C21	119.4 (3)	C52—C51—H51C	109.5
C23—C22—H22	120.3	H51A—C51—H51C	109.5
C21—C22—H22	120.3	H51B—C51—H51C	109.5
C22—C23—C24	118.9 (3)	N53—C52—C51	179.4 (5)
C22—C23—H23	120.5		
N3—RU1—N1—C1	178.0 (3)	N1—C4—C5—N3	−1.7 (4)
N7—RU1—N1—C1	−1.6 (3)	N2—C4—C5—C6	−1.3 (5)
N8—RU1—N1—C1	77.1 (3)	N1—C4—C5—C6	177.6 (3)
N4—RU1—N1—C1	176.7 (3)	N3—C5—C6—C7	−1.1 (5)
N6—RU1—N1—C1	−80.8 (3)	C4—C5—C6—C7	179.7 (3)
N3—RU1—N1—C4	0.1 (2)	C5—C6—C7—C8	−0.5 (6)
N7—RU1—N1—C4	−179.5 (2)	C6—C7—C8—C9	2.5 (6)
N8—RU1—N1—C4	−100.8 (2)	C5—N3—C9—C8	1.3 (5)
N4—RU1—N1—C4	−1.3 (4)	RU1—N3—C9—C8	179.5 (3)
N6—RU1—N1—C4	101.3 (2)	C5—N3—C9—C10	−178.7 (3)
N8—RU1—N3—C5	87.7 (3)	RU1—N3—C9—C10	−0.5 (4)
N4—RU1—N3—C5	178.4 (3)	C7—C8—C9—N3	−2.9 (5)
N6—RU1—N3—C5	−92.3 (3)	C7—C8—C9—C10	177.1 (3)
N1—RU1—N3—C5	−1.1 (3)	C11—N5—C10—N4	−2.5 (5)
N8—RU1—N3—C9	−90.5 (3)	C11—N5—C10—C9	177.4 (3)
N4—RU1—N3—C9	0.2 (3)	C13—N4—C10—N5	0.7 (5)
N6—RU1—N3—C9	89.5 (3)	RU1—N4—C10—N5	179.5 (3)
N1—RU1—N3—C9	−179.3 (3)	C13—N4—C10—C9	−179.2 (3)
N3—RU1—N4—C13	178.7 (3)	RU1—N4—C10—C9	−0.4 (4)
N7—RU1—N4—C13	−1.7 (3)	N3—C9—C10—N5	−179.4 (3)
N8—RU1—N4—C13	−80.8 (3)	C8—C9—C10—N5	0.6 (5)
N6—RU1—N4—C13	77.2 (3)	N3—C9—C10—N4	0.6 (4)
N1—RU1—N4—C13	−179.9 (2)	C8—C9—C10—N4	−179.4 (3)
N3—RU1—N4—C10	0.1 (2)	C10—N5—C11—C12	1.7 (4)
N7—RU1—N4—C10	179.7 (2)	N5—C11—C12—C13	0.7 (5)
N8—RU1—N4—C10	100.6 (2)	N5—C11—C12—CL2	−180.0 (2)
N6—RU1—N4—C10	−101.4 (2)	C10—N4—C13—C12	1.9 (4)
N1—RU1—N4—C10	1.4 (4)	RU1—N4—C13—C12	−176.7 (2)
N3—RU1—N6—C21	3.4 (3)	C11—C12—C13—N4	−2.6 (5)
N7—RU1—N6—C21	178.7 (3)	CL2—C12—C13—N4	178.1 (2)

N8—RU1—N6—C21	−176.7 (2)	C25—N6—C21—C22	−3.4 (5)
N4—RU1—N6—C21	82.9 (3)	RU1—N6—C21—C22	175.4 (2)
N1—RU1—N6—C21	−76.5 (2)	N6—C21—C22—C23	−0.8 (5)
N3—RU1—N6—C25	−177.8 (2)	C21—C22—C23—C24	3.9 (5)
N7—RU1—N6—C25	−2.5 (2)	C22—C23—C24—C25	−2.9 (5)
N8—RU1—N6—C25	2.2 (4)	C21—N6—C25—C24	4.5 (4)
N4—RU1—N6—C25	−98.3 (2)	RU1—N6—C25—C24	−174.5 (2)
N1—RU1—N6—C25	102.3 (2)	C21—N6—C25—C26	−174.9 (3)
N8—RU1—N7—C26	179.8 (2)	RU1—N6—C25—C26	6.1 (3)
N4—RU1—N7—C26	88.3 (2)	C23—C24—C25—N6	−1.3 (5)
N6—RU1—N7—C26	−2.0 (2)	C23—C24—C25—C26	178.0 (3)
N1—RU1—N7—C26	−92.4 (2)	C30—N7—C26—C27	0.2 (4)
N8—RU1—N7—C30	10.2 (2)	RU1—N7—C26—C27	−168.9 (2)
N4—RU1—N7—C30	−81.4 (2)	C30—N7—C26—C25	174.8 (3)
N6—RU1—N7—C30	−171.6 (2)	RU1—N7—C26—C25	5.7 (3)
N1—RU1—N7—C30	98.0 (2)	N6—C25—C26—N7	−7.7 (4)
N3—RU1—N8—C35	−12.3 (3)	C24—C25—C26—N7	172.9 (3)
N7—RU1—N8—C35	172.5 (3)	N6—C25—C26—C27	166.5 (3)
N4—RU1—N8—C35	−91.9 (3)	C24—C25—C26—C27	−12.9 (5)
N6—RU1—N8—C35	167.8 (2)	N7—C26—C27—C28	0.4 (5)
N1—RU1—N8—C35	67.2 (3)	C25—C26—C27—C28	−173.5 (3)
N3—RU1—N8—C31	167.6 (2)	C26—C27—C28—C29	−0.2 (5)
N7—RU1—N8—C31	−7.6 (2)	C27—C28—C29—C30	−0.4 (5)
N4—RU1—N8—C31	87.9 (2)	C26—N7—C30—C29	−0.9 (4)
N6—RU1—N8—C31	−12.3 (4)	RU1—N7—C30—C29	168.3 (2)
N1—RU1—N8—C31	−112.9 (2)	C26—N7—C30—C31	−179.7 (3)
C4—N1—C1—C2	1.8 (4)	RU1—N7—C30—C31	−10.6 (3)
RU1—N1—C1—C2	−176.1 (2)	C28—C29—C30—N7	1.0 (5)
N1—C1—C2—C3	−3.1 (5)	C28—C29—C30—C31	179.6 (3)
N1—C1—C2—CL1	175.5 (3)	C35—N8—C31—C32	3.9 (4)
C4—N2—C3—C2	1.5 (4)	RU1—N8—C31—C32	−176.0 (2)
C1—C2—C3—N2	1.5 (5)	C35—N8—C31—C30	−175.6 (3)
CL1—C2—C3—N2	−177.1 (2)	RU1—N8—C31—C30	4.5 (3)
C3—N2—C4—N1	−3.0 (4)	N7—C30—C31—N8	3.6 (4)
C3—N2—C4—C5	175.8 (3)	C29—C30—C31—N8	−175.1 (3)
C1—N1—C4—N2	1.3 (4)	N7—C30—C31—C32	−175.9 (3)
RU1—N1—C4—N2	179.6 (2)	C29—C30—C31—C32	5.4 (5)
C1—N1—C4—C5	−177.4 (3)	N8—C31—C32—C33	−2.8 (5)
RU1—N1—C4—C5	0.8 (3)	C30—C31—C32—C33	176.7 (3)
C9—N3—C5—C6	0.7 (6)	C31—C32—C33—C34	0.0 (5)
RU1—N3—C5—C6	−177.5 (3)	C32—C33—C34—C35	1.6 (5)
C9—N3—C5—C4	180.0 (3)	C31—N8—C35—C34	−2.3 (5)
RU1—N3—C5—C4	1.8 (4)	RU1—N8—C35—C34	177.6 (2)
N2—C4—C5—N3	179.5 (3)	C33—C34—C35—N8	−0.5 (5)

Fig. 1


Cl1
C3
C2
N2
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C31
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C9
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N5
C10
C13
N5
C12
C11
Cl2