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# Bis[2,4-bis(2-pyridyl-κ*N*)-6-(4-pyridyl)-1,3,5-triazine-κ$N^3$]ruthenium(II) bis(hexafluorophosphate)

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The coordination of Ru in the title compound, $[Ru(C_{18}H_{12}N_6)_2](PF_6)_2$, is octahedral. The coordination sphere is formed by six N atoms from the tridentate sites of two ligands that are meridionally oriented around the $Ru^{II}$ ion. The locations of the donor atoms deviate substantially from an ideal octahedron. The Ru—N distances are in the range 1.983 (4)–2.111 (4) Å. The Ru atom occupies a special position with twofold rotational symmetry. One of the P atoms occupies a special position with twofold rotational symmetry and the other P atom is located on a special position at a centre of symmetry.

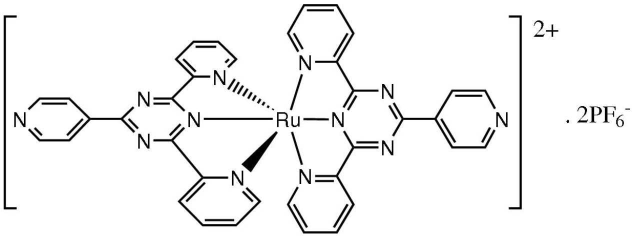
**Key indicators**

Single-crystal X-ray study
*T* = 85 K
Mean σ(C–C) = 0.008 Å
*R* factor = 0.058
*wR* factor = 0.137
Data-to-parameter ratio = 13.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

Our aim involves the synthesis and characterization of bridging ligands containing two non-equivalent binding sites. Our interests are particularly focused on preparation of such ligands capable of binding an $Ru^{II}$ ion at one site and a $Co^{III}$ ion at the other site. As part of our study, the ligand 2,4-bis(2-pyridyl)-6-(4-pyridyl)-1,3,5-triazine was synthesized using the method of Polson *et al.* (2002). This terpyridyl-like ligand, which contains a remote fourth N-donor atom, was a candidate for our study. The title ruthenium complex, (I), in which two ligands are coordinated to an $Ru^{II}$ ion through their tridentate sites was prepared according to the reported methods (Polson *et al.*, 2002, 2004).



(I)

Complex (I) (Fig. 1) crystallizes in the orthorhombic space group *Pcca* with four well separated molecules in the unit cell. The asymmetric unit comprises one half-cation and two half-anions. The Ru atom occupies a special position with twofold rotational symmetry. One of the P atoms occupies a special position with twofold rotational symmetry and the other P atom is located on a special position at a centre of symmetry. The ruthenium ion is six-coordinate, but the geometry is significantly distorted from that of an ideal octahedron as a result of the constraints enforced by the ligand structure. This is commonly observed for terpyridyl-like ligands (Thummel &

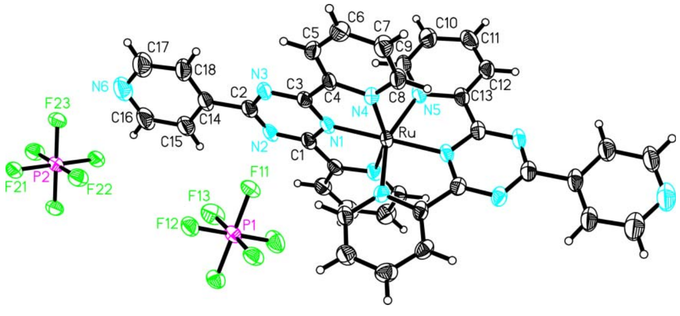


**Figure 1**
A perspective view of the $Ru^{II}$ complex (I), showing the atom-labelling scheme with 50% probability displacement ellipsoids. Unlabelled atoms in the cation and $PF_6^-$ anions $P_1$ and $P_2$ are related by the symmetry codes ($\frac{1}{2} - x, -y, z$), ($\frac{1}{2} - x, 1 - y, z$) and ($1 - x, 2 - y, -z$), respectively. H atoms are drawn as small spheres of arbitrary radii.

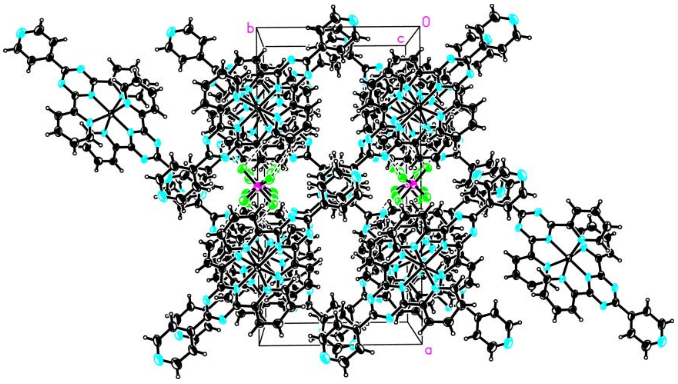


**Figure 2**
A packing diagram, showing the $\pi$–$\pi$ stacking interactions between the complexes parallel to the *ac* plane.

Jahng, 1986; Constable *et al.*, 1990, 1992, 2001; Cathey *et al.*, 1990; Bushell *et al.*, 1998; Craig *et al.*, 1998; Sasaki *et al.*, 1998; Cardenas *et al.*, 1999; Chamchoumis & Potvin, 1999; Fallahpour *et al.*, 1999; Lashgari *et al.*, 1999; Pyo *et al.*, 1999; Ziegler *et al.*, 1999; Alcock *et al.*, 2000; Encinas *et al.*, 2002; Fang *et al.*, 2002; Laine *et al.*, 2002). Each of the tridentate ligands occupies three meridionally located coordination sites. The Ru—N bond lengths show the expected pattern for complexes related to $[Ru(terpy)_2](PF_6)_2$ (Pyo *et al.*, 1999; Lashgari *et al.*, 1999), with short metal–ligand bonds to the central ring [1.983 (4) Å] and longer bonds to the side pyridine rings [mean 2.108 (4) Å]. The non-coordinated pyridine rings are not coplanar with the central triazine ring and form interannular angles of 16.8 (3)°. Similar observations have been made for the $Ni^{II}$ and $Ru^{II}$ complexes based on the 4′-phenyl-substituted terpyridine system (Constable *et al.*, 1990; Chamchoumis *et al.*, 1999). As shown in Fig. 2, there are $\pi$–$\pi$ stacking interactions (face–face) between the terminal pyridyl rings of adjacent complexes [centroid–centroid distance = 3.72 (8) Å]. The complex cations are arranged like the steps of a spiral staircase along the *b* axis of the unit cell, with the stack of pyridyl rings forming the pole of the staircase. There appears to be no significant hydrogen bonding in the crystal structure.

## Experimental

The 2,4-bis(2-pyridyl)-6-(4-pyridyl)-1,3,5-triazine ligand and its ruthenium complex, (I), were synthesized according to the methods of Polson *et al.* (2002, 2004). Red block-shaped crystals were obtained by slow evaporation of a $CH_3CN$–$H_2O$ solution of the complex (yield 16%).

*Crystal data*

$[Ru(C_{18}H_{12}N_6)_2](PF_6)_2$
$M_r = 1015.68$
Orthorhombic, *Pcca*
$a = 21.474$ (11) Å
$b = 11.008$ (6) Å
$c = 16.044$ (8) Å
$V = 3793$ (3) Å$^3$
$Z = 4$
$D_x = 1.779$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 8243 reflections
$\theta = 4.9$–$52.5°$
$\mu = 0.61$ mm$^{-1}$
$T = 85$ (2) K
Block, red
0.61 × 0.29 × 0.08 mm

*Data collection*

Bruker SMART CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.709$, $T_{max} = 0.953$
21 050 measured reflections

3864 independent reflections
2935 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 26.4°$
$h = -26 \rightarrow 26$
$k = -13 \rightarrow 11$
$l = -18 \rightarrow 19$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.137$
$S = 1.16$
3864 reflections
287 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 19.9599P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.54$ e Å$^{-3}$
$\Delta\rho_{min} = -1.09$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ru—N1 | 1.983 (4) | Ru—N5 | 2.111 (4) |
| Ru—N4 | 2.104 (4) | | |
| $N1^i$—Ru—N1 | 178.9 (3) | N1—Ru—$N5^i$ | 77.41 (18) |
| $N1^i$—Ru—$N4^i$ | 77.00 (17) | $N4^i$—Ru—$N5^i$ | 92.97 (17) |
| N1—Ru—$N4^i$ | 102.22 (16) | N4—Ru—$N5^i$ | 154.38 (16) |
| N1—Ru—N4 | 77.00 (17) | $N1^i$—Ru—N5 | 77.41 (18) |
| $N4^i$—Ru—N4 | 93.6 (2) | $N5^i$—Ru—N5 | 91.7 (2) |
| $N1^i$—Ru—$N5^i$ | 103.38 (17) | | |
| N3—C2—C14—C18 | 16.9 (8) | N2—C2—C14—C15 | 16.2 (8) |

Symmetry code: (i) $\frac{1}{2} - x, -y, z$.

All H atoms were placed in calculated positions [C—H = 0.93 Å and $U_{iso} = 1.2U_{eq}$(C)] and were included in the refinement in the riding-model approximation. The highest peak is very close to Ru (0.89 Å) and the deepest hole is near N4 (1.62 Å), neither in chemically sensible locations for atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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**m982** Richard M. Hartshorn *et al.* • $[Ru(C_{18}H_{12}N_6)_2](PF_6)_2$ *Acta Cryst.* (2005). E**61**, m981–m983

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