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Acetonitrile(1,10-phenanthroline)(2,2′:6′,2″-terpyridine)ruthenium(II) bis(hexafluorophosphate)

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Key indicators

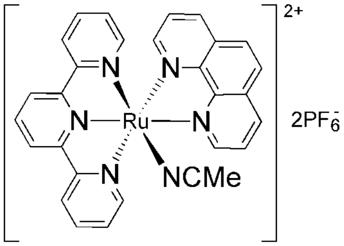
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.012 Å
R factor = 0.089
wR factor = 0.172
Data-to-parameter ratio = 8.4

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

The asymmetric unit of the title compound, [Ru(C_2H_3N)(phen)(terpy)](PF_6)$_2$ [phen is 1,10-phenanthroline ($C_{12}H_8N_2$) and terpy is 2,2′:6′,2″-terpyridine ($C_{15}H_{11}N_3$)] contains a monomeric [Ru(CH_3CN)(phen)(terpy)]$^{2+}$ cation and two hexafluorophosphate anions. The ligand environment about the Ru atom is distorted octahedral. The Ru—N distances are in the range 1.933 (5)–2.083 (5) Å and the Ru—N(acetonitrile) distance is 2.016 (7) Å.

Comment

The chemistry of [Ru(bpy)$_3$]$^{2+}$ and its derivatives has received considerable attention due to a unique combination of photochemistry, electrochemistry and chemical stability. These complexes are also promising candidates for ideal photocatalysts for the visible-light photo-induced decomposition of water into dihydrogen and dioxygen. Recently, metal–polypyridine complexes have been widely used as building blocks. In particular, the occurrence of isomers is a major problem in the design of supramolecular systems by the synthetic assembly of mononuclear building blocks. From a structural point of view, the terpyridine (terpy) ligand is superior to the bidentate ligand bpy. For the design of Ru^{II} terpyridine complexes, our aim was to prepare monoterpyridine complexes using ancillary ligands.



(I)

The title compound, (I), was synthesized and isolated. The ligand environment about the Ru atom is distorted octahedral; the terpy ligand is coordinated in a meridional fashion, the phen ligand is coordinated in a *cis* fashion and the N atom from the acetonitrile molecule is *trans* to one of the phen N atoms. The largest distortion of the octahedral geometry is due to the geometrical constraints of the terpy ligand, which exhibits small N—Ru—N angles [N1—Ru—N2 = 79.0 (2)°, N3—Ru—N4 = 80.3 (2)° and N4—Ru—N5 = 78.9 (2)°] and an Ru—N distance for the central pyridyl ring fragment of 1.933 (5) Å, which is shorter than those involving the N atoms of the outer two pyridyl rings. These values are in good agreement with those reported for iridium(III) and ruthenium(II) complexes of the terpy ligand (Yoshikawa *et al.*, 2003; Spek *et al.*, 1994).

Experimental

The desired complex was prepared by a sequential procedure with ligand replacement. $[RuCl_3]\cdot H_2O$ (0.5 mmol) and 2,2′:6′,2″-terpyridine (0.5 mmol) were mixed in ethylene glycol (15 ml). The suspended mixture was refluxed for 5 min in a microwave oven under a purging nitrogen atmosphere. 1,10-Phenanthroline (0.5 mmol) was added to the red solution under reflux over a period of 10 min. The mixture was then cooled to room temperature. A saturated aqueous solution of KPF_6 (20 ml) was added as a counter-ion. A black–red product began to precipitate and was collected by vacuum filtration. Dark red single crystals were obtained by recrystallization from acetonitrile.

Crystal data

$[Ru(C_2H_3N)(C_{12}H_8N_2)(C_{15}H_{11}N_3)](PF_6)_2$
$M_r = 845.53$
Triclinic, $P\overline{1}$
$a = 8.7861$ (3) Å
$b = 10.3590$ (9) Å
$c = 17.9636$ (7) Å
$\alpha = 99.192$ (7)°
$\beta = 90.389$ (2)°
$\gamma = 105.774$ (3)°
$V = 1551.0$ (2) Å^3

$Z = 2$
$D_x = 1.810$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9574 reflections
$\theta = 1.1$–30.4°
$\mu = 0.72$ mm^{-1}
$T = 296.2$ K
Platelet, red
0.2 × 0.2 × 0.1 mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
ω scans
Absorption correction: multi-scan, (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.707$, $T_{max} = 0.931$
14 369 measured reflections

8594 independent reflections
3776 reflections with $I > 2\sigma(I)$
$R_{int} = 0.110$
$\theta_{max} = 30.5°$
$h = -12 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.172$
$S = 1.29$
3776 reflections
451 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.031$
$\Delta\rho_{max} = 0.84$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—N1	2.083 (5)	Ru1—N5	2.075 (5)
Ru1—N2	2.054 (6)	Ru1—N6	2.016 (7)
Ru1—N3	2.050 (6)	N6—C28	1.13 (1)
Ru1—N4	1.933 (5)		
N1—Ru1—N2	79.0 (2)	N2—Ru1—N6	172.3 (2)
N1—Ru1—N3	96.2 (2)	N3—Ru1—N4	80.3 (2)
N1—Ru1—N4	172.9 (3)	N3—Ru1—N5	159.2 (2)
N1—Ru1—N5	104.4 (2)	N3—Ru1—N6	91.4 (2)
N1—Ru1—N6	93.8 (2)	N4—Ru1—N5	78.9 (2)
N2—Ru1—N3	91.8 (2)	N4—Ru1—N6	92.6 (2)
N2—Ru1—N4	94.8 (2)	N5—Ru1—N6	89.6 (2)
N2—Ru1—N5	89.8 (2)	N6—C28—C29	178.4 (8)

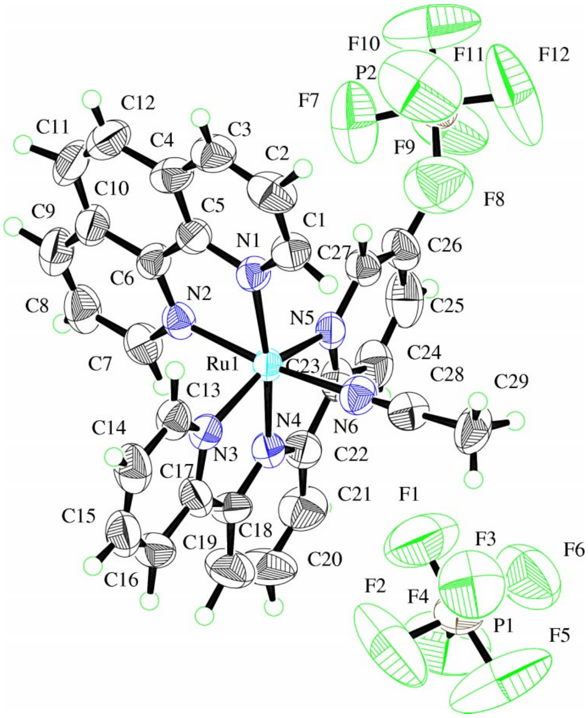


Figure 1
The molecular structure of the title compound, shown with 50% probability displacement ellipsoids.

All H atoms bonded to carbon were placed at calculated positions, with isotropic displacement parameters (C—H = 0.90–1.04 Å). The H atoms bonded to nitrogen were placed geometrically. The maximum and minimum electon-density peaks are 0.84 and 0.58 Å, respectively, from atom F11 and N3. The high R_{int} value is a result of the poor quality of the crystal used.

Data collection: *PROCESS-AUTO* (Molecular Structure Corporation and Rigaku, 2000); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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