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Bis(2,2′-bipyridine)(3,8-diethynyl-1,10-phenanthroline)ruthenium(II) bis(hexafluorophosphate) diethyl ether disolvate

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The asymmetric unit of the title compound, $[Ru(C_{10}H_8N_2)_2(C_{16}H_8N_2)](PF_6)_2\cdot 2Et_2O$ or $[Ru(bipy)_2(dephen)](PF_6)_2\cdot 2Et_2O$, where bipy is 2,2′-bipyridine and dephen is 3,8-diethynyl-1,10-phenanthroline, contains a monomeric [Ru(bipy)$_2$(dephen)] cation, two hexafluorophosphate anions, and two molecules of diethyl ether. The ruthenium(II) ion is in a distorted octahedral environment, coordinated by two bipy and one dephen ligands. Weak intermolecular C—H···F hydrogen bonds are observed in the crystal structure.

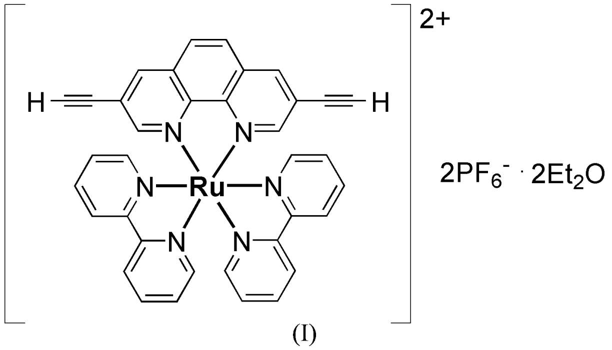
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.011 Å
Disorder in solvent or counterion
R factor = 0.099
wR factor = 0.189
Data-to-parameter ratio = 15.9

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

Comment

There has been increasing interest in the design of multinuclear systems built up from photo-active ruthenium(II)–polypyridyl complexes as a result of the development of photonic and opto-electronic devices. In this regard, numerous substituted 2,2′-bipyridine and 1,10-phenanthroline compounds have been synthesized and used as multidentate ligands. Recently, 3,8-diethynyl-1,10-phenanthroline (dephen) and its derivatives have become popular in the field of luminescent materials (Schmittel *et al.*, 2005; Ziessel, Grosshenny *et al.*, 2004). To the best of our knowledge, no example of the molecular structure of a ruthenium(II)–polypyridyl complex containing the dephen ligand has been reported, although this type of ruthenium–polypyridyl complex has been widely used over the past decade as the starting material in photophysical and electrochemical studies of new photoactive supramolecular compounds (Ulrich & Ziessel, 2004; Shiotsuka *et al.*, 2002; Tzalis & Tor, 1997). Here we report the synthesis and the crystal structure of the title new ruthenium(II)–polypyridyl complex, (I).



(I)

The asymmetric unit of (I) consists of an [Ru(bipy)$_2$(dephen)] cation (Fig. 1) (bipy is 2,2′-bipyridine and dephen is 3,8-diethynyl-1,10-phenanthroline), two hexafluorophosphate anions and two diethyl ether solvent molecules. The coordination environment around the Ru^{II} atom is distorted octahedral, with *trans* angles at the Ru^{II} site ranging from 171.1 (2)

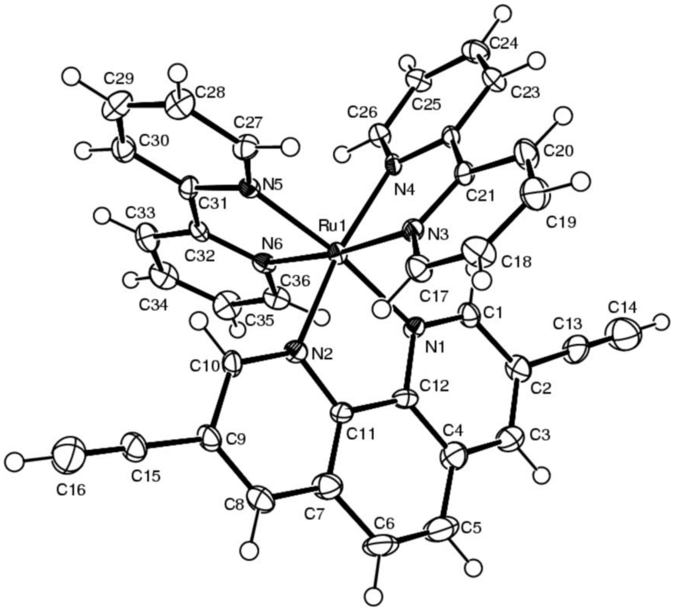


Figure 1
The structure of the cation of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

to 173.7 (2)° (Table 1). The average Ru—N bond length [2.061 (5) Å] involving the bipyridine ligands is shorter than that [2.071 (5) Å] with phenanthroline (Table 1). The ligand bite angle, N—Ru—N, of bipyridine [78.6 (2)°] is smaller than that of phenanthroline [80.26 (19)°]. These tendencies are consistent with the results reported for $[Ru(bipy)_3](PF_6)_2$ [2.056 (2) Å and 78.7 (1)°; Rillema *et al.*, 1992] and $[Ru(phen)_3](PF_6)_2$ [2.063 (4) Å and 79.8 (2)°; Breu & Stoll, 1996; phen = 1,10-phenanthroline].

Weak intermolecular C—H···F hydrogen bonds (Table 2) stabilize the crystal packing along with van der Waals forces.

Experimental

3,8-Diethynyl-1,10-phenanthroline was synthesized according to the method of Ziessel & Stroh (2004). The ruthenium complex $RuCl_2(bipy)_2$ was prepared according to the method of Sullivan *et al.* (1978). Dephen (460 mg, 2.02 mmol) and $RuCl_2(bipy)_2$ (1092 mg, 2.10 mmol) were heated at 363 K in a mixture of ethanol (200 ml) and water (20 ml) for 12 h. After filtration of the solution, the filtrate was concentrated and added to water (70 ml) containing NH_4PF_6 (1980 mg, 12.2 mmol). A red precipitate was collected by suction filtration, washed with water (50 ml) and diethyl ether (50 ml), and dried at 303 K under vacuum for 12 h. Orange crystals suitable for X-ray structure investigations were obtained from a solution in acetonitrile–diethyl ether (1:1).

Crystal data

$[Ru(C_{10}H_8N_2)_2(C_{16}H_8N_2)](PF_6)_2\cdot 2C_4H_{10}O$
$M_r = 1079.86$
Triclinic, $P\bar{1}$
$a = 11.617$ (2) Å
$b = 14.385$ (3) Å
$c = 14.388$ (3) Å
$\alpha = 84.413$ (12)°
$\beta = 79.423$ (11)°
$\gamma = 80.166$ (11)°
$V = 2323.4$ (8) Å^3
$Z = 2$
$D_x = 1.544$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.50$ mm^{-1}
$T = 120$ (2) K
Plate, orange
0.31 × 0.22 × 0.07 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Spek, 2003)
$T_{min} = 0.861$, $T_{max} = 0.966$
23098 measured reflections
10281 independent reflections
8528 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.099$
$wR(F^2) = 0.189$
$S = 1.19$
10281 reflections
645 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 19.3492P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -1.02$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—Ru1	2.075 (5)	N4—Ru1	2.062 (5)
N2—Ru1	2.066 (5)	N5—Ru1	2.060 (5)
N3—Ru1	2.057 (5)	N6—Ru1	2.063 (5)
N3—Ru1—N5	97.0 (2)	N4—Ru1—N2	171.1 (2)
N3—Ru1—N4	78.6 (2)	N6—Ru1—N2	89.9 (2)
N5—Ru1—N4	92.98 (19)	N3—Ru1—N1	87.0 (2)
N3—Ru1—N6	173.7 (2)	N5—Ru1—N1	173.1 (2)
N5—Ru1—N6	78.6 (2)	N4—Ru1—N1	93.36 (19)
N4—Ru1—N6	97.15 (19)	N6—Ru1—N1	97.9 (2)
N3—Ru1—N2	94.8 (2)	N2—Ru1—N1	80.26 (19)
N5—Ru1—N2	93.73 (19)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···F21	0.95	2.46	3.204 (7)	135
C5—H5···F2	0.95	2.43	3.312 (8)	154
C14—H14···F4A^{i}	0.95	2.37	3.29 (3)	163
C14—H14···F4B^{i}	0.95	2.21	3.161 (19)	174
C16—H16···F5A^{ii}	0.95	2.19	3.143 (18)	175
C16—H16···F5B^{ii}	0.95	2.39	3.30 (2)	161
C19—H19···F3B^{iii}	0.95	2.36	3.10 (2)	134
C20—H20···F25^{iv}	0.95	2.39	3.336 (8)	177
C23—H23···F25^{iv}	0.95	2.43	3.384 (8)	178
C33—H33···F24^{v}	0.95	2.38	3.334 (8)	177
C34—H34···F6A^{vi}	0.95	2.33	3.16 (3)	145
C34—H34···F6B^{vi}	0.95	2.40	3.056 (17)	126

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x, -y+1, -z+1$; (iv) $-x+1, -y+1, -z$; (v) $-x+1, -y, -z$; (vi) $-x+1, -y, -z+1$.

All H atoms were included in calculated positions, with C—H = 0.95 or 0.98 Å, and treated as riding with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$. Four F atoms in one of the two hexafluorophosphate anions are rotationally disordered (the approximate axis of rotation is F1—P2—F2) between two positions with the F*nA*—P2—F*nB* (*n* = 3–6) angles in the range 23.6–30.4° and refined occupancies of 0.51 (5) and 0.49 (5). The deepest hole is located 0.92 Å from atom Ru1.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

Acta Cryst. (2006). E**62**, m1410–m1412 Shiotsuka *et al.* • $[Ru(C_{10}H_8N_2)_2(C_{16}H_8N_2)](PF_6)_2\cdot 2Et_2O$ **m1411**

ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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m1412 Shiotsuka *et al.* • $[Ru(C_{10}H_8N_2)_2(C_{16}H_8N_2)](PF_6)_2\cdot 2Et_2O$ *Acta Cryst.* (2006). E**62**, m1410–m1412