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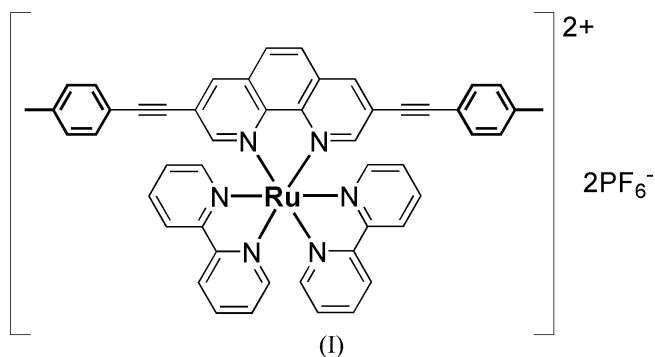# Bis(2,2'-bipyridine){3,8-bis[2-(4-tolyl)-ethynyl]-1,10-phenanthroline}ruthenium(II) bis(hexafluorophosphate)

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The asymmetric unit of the title compound, $[Ru(C_{10}H_8N_2)_2(C_{30}H_{20}N_2)](PF_6)_2$, contains a monomeric $[Ru(bpy)_2(dtephen)]$ cation {bpy is 2,2'-bipyridine and dtephen is 3,8-bis[2-(4-tolyl)ethynyl]-1,10-phenanthroline} and two hexafluorophosphate anions. The ruthenium(II) ion is in a distorted octahedral environment coordinated by two bpy ligands and one dtephen ligand. The dtephen ligand is almost planar. π–π stacking interactions and C—H···F hydrogen bonds are observed in the crystal structure.

Comment

Ruthenium(II) polypyridyl complexes have played an important role in the development of photoactive molecular systems. In this regard, many multisubstituted 2,2'-bipyridines (bpy) and 1,10-phenanthrolines (phen) have been designed and synthesized. Recently, conjugated 1,10-phenanthrolines substituted with arylenes at the 3,8-positions have attracted much interest in the field of luminescence and materials chemistry; these compounds have unusual photophysical properties because of the enhanced electronic delocalization (Joshi *et al.*, 1999; Birckner *et al.*, 2001; Ulrich & Ziessel, 2004). No example of the molecular structure of a ruthenium polypyridyl complex containing 3,8-bis(arylarene)-1,10-phenanthroline or its derivatives has been reported and only one example of a complex with 3,5,6,8-tetrakis(phenylethynyl)-1,10-phenanthroline coordinated to zinc dichloride (Rau *et al.*, 2004) has been reported, although many kinds of ruthenium polypyridyl complexes have been reported during the past decade (Tzalis & Tor, 1995; Connors *et al.*, 1998; Soutiriou-Leventis *et al.*, 2004; Leventis *et al.*, 2004). Here, we report the synthesis and the crystal structure of the title ruthenium(II) polypyridyl complex, (I).

The asymmetric unit of (I) consists of an $[Ru(bpy)_2(dtephen)]$ cation {dtephen is 3,8-bis[2-(4-tolyl)ethynyl]-1,10-phenanthroline} (Fig. 1) and two hexafluorophosphate anions.
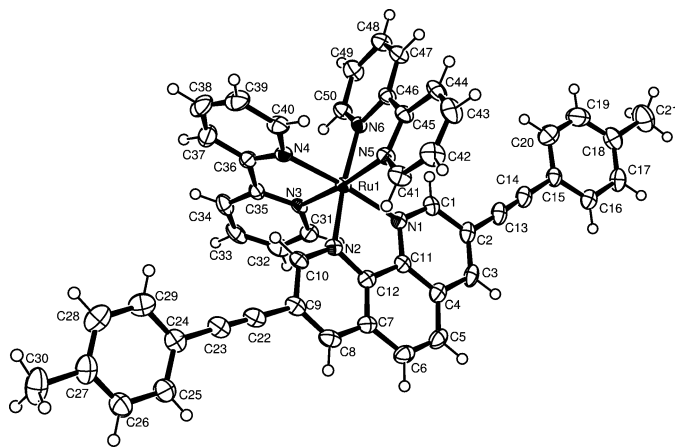
Figure 1
The structure of the cation of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The ligand environment around the Ru^{II} atom is distorted octahedral, with *trans* angles at the Ru^{II} site in the range 173.92 (11)–175.19 (11)° (Table 1). The average Ru—N bond length [2.046 (3)Å] of bpy is shorter than that [2.061 (3)Å] of phenanthroline. The average ligand bite angle, N—Ru—N, of bpy [78.88 (11)°] is smaller than that of phenanthroline [79.45 (11)°]. These differences are consistent with the results for [Ru(bpy)₃](PF₆)₂ [2.056 (2)Å and 78.7 (1)°; Rillema *et al.*, 1992] and [Ru(phen)₃](PF₆)₂ [2.063 (4)Å and 79.8 (2)°; Breu & Stoll, 1996].

The most interesting feature of the crystal structure is the near-planarity of the dtephen ligand. The planes of the C15–C20 and C24–C29 benzene rings form dihedral angles of 6.2 (1) and 13.6 (1)°, respectively, with the plane of the phenanthroline ring system. It seems reasonable to consider that the planarity is induced by crystal packing forces because intermolecular overlaps between dtephen ligands in neighbouring cations are observed in the crystal structure. The centroid–centroid distances between ovelapped rings are: $Cg1\cdots Cg2(1 - x, 1 - y, -z) = 3.739$ (3)Å and $Cg1\cdots Cg3(2 - x, 1 - y, 1 - z) = 3.776$ (3)Å, where $Cg1$, $Cg2$ and $Cg3$ denote the centroids of the C4–C7/C11/C12, C15–C20 and C24–C29 rings, respectively. In addition, there are several C—H···F hydrogen bonds (Table 2).

Experimental

3,8-Bis[2-(4-tolyl)ethynyl]-1,10-phenanthroline (dtephen) was synthesized by the method of Tzalis & Tor (1995) and the ruthenium complex Ru(bpy)₂Cl₂ was prepared according to the method of Sullivan *et al.* (1978). Dtephen (150 mg, 0.37 mmol) and Ru(bpy)₂Cl₂ (193 mg, 0.37 mmol) were refluxed in ethanol solution (45 ml) for 5 h. After filtration of the solution, the filtrate was concentrated and added to water (50 ml) containing NH₄PF₆ (241 mg, 1.48 mmol). An orange precipitate was collected by suction filtration, washed with water (50 ml) and ether (50 ml), and dried at 303 K under vacuum for 12 h. Orange crystals suitable for X-ray structure investigation were obtained from a solution in acetonitrile–ethanol (1:1). Analysis calculated for C₅₀H₃₆F₁₂N₆P₂Ru: C 54.01, H 3.26, N 7.56%; found: C 53.82, H 3.36, N, 7.62%. ¹H NMR (CD₃CN): δ 8.70 (*d*, *J* = 1.6 Hz, 2H,

phen-H2 and -H9), 8.53 (*m*, 4H, bpy-H6′ and -H6), 8.23 (*s*, 2H, phen-H5 and -H6), 8.17 (*d*, *J* = 1.6 Hz, 2H, phen-H4 and -H7), 8.10 (*m*, 2H, bpy-H5′), 8.03 (*m*, 2H, bpy-H5), 7.81 (*m*, 2H, bpy-H3′), 7.64 (*m*, 2H, bpy-H3), 7.45 (*m*, 2H, bpy-H4′), 7.43 (*d*, *J* = 8.1 Hz, 4H, tolyl-H3 and -H5), 7.27 (*m*, 2H, bpy-H4), 7.26 (*d*, *J* = 8.1 Hz, 4H, tolyl-H2 and -H6), 2.37 (*s*, 6H, tolyl-CH₃).

Crystal data

[Ru(C₁₀H₈N₂)₂(C₃₀H₂₀N₂)](PF₆)₂	$V = 2381.0$ (3) Å³
$M_r = 1111.86$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.551$ Mg m⁻³
$a = 11.284$ (1) Å	Synchrotron radiation
$b = 13.083$ (1) Å	$\lambda = 0.3282$ Å
$c = 17.760$ (1) Å	$\mu = 0.28$ mm⁻¹
$\alpha = 98.922$ (3)°	$T = 120$ (2) K
$\beta = 94.625$ (2)°	Plate, orange
$\gamma = 111.605$ (4)°	0.14 × 0.12 × 0.02 mm

Data collection

MacScience DIP LABO diffractometer	24479 measured reflections
ω scans	13149 independent reflections
Absorption correction: multi-scan (*PLATON*; Spek, 2003)	9834 reflections with $I > 2\sigma(I)$
$T_{min} = 0.962$, $T_{max} = 0.994$	$R_{int} = 0.059$
	$\theta_{max} = 13.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$+ 4.6215P]$
$wR(F^2) = 0.127$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
13149 reflections	$\Delta\rho_{max} = 1.27$ e Å⁻³
640 parameters	$\Delta\rho_{min} = -0.78$ e Å⁻³
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

N1—Ru1	2.061 (3)	N4—Ru1	2.046 (3)
N2—Ru1	2.061 (3)	N5—Ru1	2.037 (2)
N3—Ru1	2.049 (2)	N6—Ru1	2.053 (3)
N5—Ru1—N4	96.83 (11)	N3—Ru1—N2	88.71 (10)
N5—Ru1—N3	173.92 (11)	N6—Ru1—N2	174.07 (10)
N4—Ru1—N3	78.78 (11)	N5—Ru1—N1	86.89 (10)
N5—Ru1—N6	79.00 (11)	N4—Ru1—N1	175.19 (11)
N4—Ru1—N6	86.83 (11)	N3—Ru1—N1	97.72 (10)
N3—Ru1—N6	96.45 (10)	N6—Ru1—N1	96.90 (11)
N5—Ru1—N2	96.06 (10)	N2—Ru1—N1	79.44 (11)
N4—Ru1—N2	97.08 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···F4	0.95	2.38	3.070 (6)	130
C8—H8···F9^i	0.95	2.40	3.287 (5)	154
C10—H10···F7^{ii}	0.95	2.38	2.996 (5)	122
C33—H33···F8^{iii}	0.95	2.53	3.403 (5)	154
C34—H34···F7^{iii}	0.95	2.50	3.308 (5)	142
C39—H39···F8^{iv}	0.95	2.33	3.229 (5)	157
C43—H43···F5^{ii}	0.95	2.49	3.369 (6)	154
C44—H44···F1^{ii}	0.95	2.28	3.046 (6)	137
C47—H47···F2^v	0.95	2.36	3.152 (6)	140
C48—H48···F4^v	0.95	2.47	3.343 (6)	153

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

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H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.95 or 0.98 Å and $U_{iso}(H) = 1.2$ or 1.5 times $U_{eq}(C)$. A *PLATON* analysis (Spek, 2003) indicated that the crystal structure of (I) contains solvent-accessible voids at three independent locations in the unit cell, with volumes of 50, 69 and 69 Å^3. The total electron count in these voids is 7, indicating the possible presence of a water molecule with partial occupancy. The highest residual electron-density peak is 0.51 Å from atom Ru1.

Data collection: *DIP XPRESS* (MacScience, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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