Chloro(4,7-diphenyl-1,10-phenanthroline)-(2,2':6',2''-terpyridine)ruthenium(II) hexafluorophosphate

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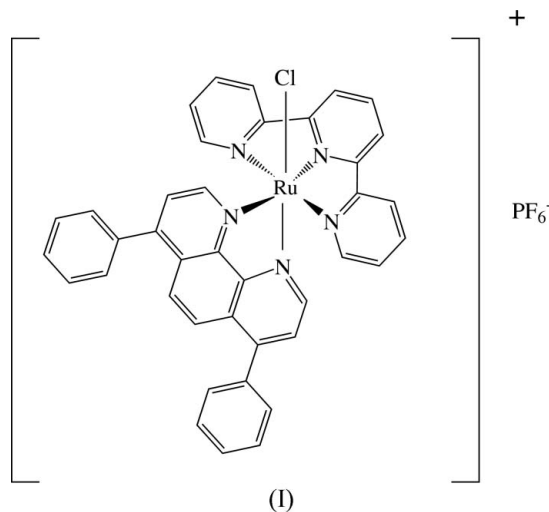
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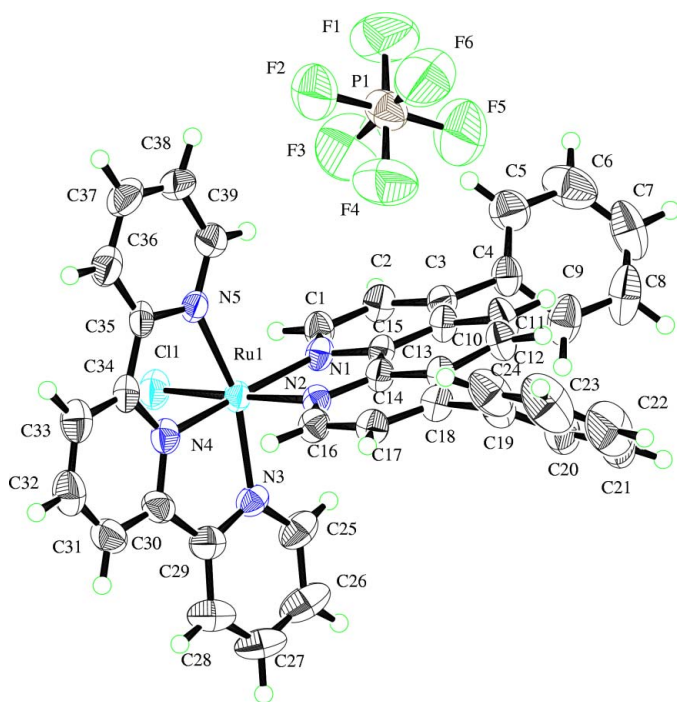The title compound, $[RuCl(C_{24}H_{16}N_2)(C_{15}H_{11}N_3)]PF_6$, consists of a monomeric Ru^{II} complex cation and a hexafluorophosphate anion. The coordination environment about the Ru^{II} atom is distorted octahedral, where the 2,2':6',2''-terpyridine (terpy) ligand is coordinated in a meridional fashion, the 4,7-diphenyl-1,10-phenanthroline (dpphen) ligand is coordinated in a *cis* fashion and the Cl atom is *trans* to one of the dpphen N atoms. The Ru—N bond distances are in the range 1.956 (5)–2.096 (5) Å and the Ru—Cl distance is 2.403 (2) Å.

Comment

Ruthenium(II) complexes have been widely studied within the field of inorganic chemistry. Ru^{II} polypyridine complexes play outstanding roles in the fields of solar energy conversion and the storage of light. The chemistry of $Ru(bpy)_3^{2+}$ and its derivatives has been most studied. Metal polypyridine complexes are widely used as building blocks. However, the occurrence of isomers is a major problem in the design of supramolecular systems by synthetic assembly of mononuclear building blocks. The terpyridine ligand is superior to bipyridine from a structural point of view. We tried to synthesize several Ru^{II} complexes with mixtures of a terpyridine ligand and 4,7-diphenyl-1,10-phenanthroline (dpphen) for the design of Ru^{II} terpyridine complexes (Yoshikawa *et al.*, 2004). In the present study, the title compound, (I), [RuCl(dpphen)(terpy)]PF_6, was synthesized and isolated.

(I)

In (I), the environment about the Ru atom is distorted octahedral; the terpy ligand is coordinated in a meridional

Figure 1
Molecular structure of (I), showing 50% probability displacement ellipsoids.

fashion, and the dpphen ligand is coordinated in a *cis* fashion with the Cl atom *trans* to one of the dpphen N atoms. The largest distortion of the octahedral geometry is due to the geometric constraints of the terpy ligand, which exhibits small N—Ru—N angles [N3—Ru1—N4 = 80.5 (2)° and N4—Ru1—N5 = 79.4 (2)°] and an Ru—N distance for the central pyridyl ring fragment [1.956 (5) Å] shorter than those for the outer two. These values are in good agreement with those of other Ir^{III} and Ru^{II} complexes with the terpy ligand (Yoshikawa *et al.*, 2003; Spek *et al.*, 1994). The Ru—N bond distances of 2.028 (4)–2.096 (5) Å for the dpphen ligand and 2.042 (5)–2.057 (5) Å for the two terminal terpy ring fragments are in the range found for the other Ru^{II} complexes with polypyridyl ligands. The two Ru—N$_{dpphen}$ bond lengths are significantly different, since N1 is *trans* to the sterically contracted atom N4, and N2 is *trans* to the chloride ion. The tendency for the bond length between the Ru^{II} and N atom *trans* to the central terpy ring to become longer is also observed in [RuCl(terpy)(2,2′-biquinoline)]PF$_6$ (Spek *et al.*, 1994).

Experimental

The desired complex was prepared by a sequential procedure with ligand replacement. [RuCl$_3$]·H$_2$O (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. 4,7-Diphenyl-1,10-phenanthroline (0.5 mmol) was added to the refluxing red solution for 10 min. The mixture was then cooled to room temperature. A saturated aqueous solution of KPF$_6$ (20 ml) was added, and a black–red product began to precipitate and was collected by vacuum filtration (yield 75%).

Dark-red crystals of (I) were obtained by recrystallization from acetonitrile.

Table 1
Selected geometric parameters (Å, °).

Ru1—Cl1	2.403 (2)	Ru1—N3	2.042 (5)
Ru1—N1	2.096 (5)	Ru1—N4	1.956 (5)
Ru1—N2	2.028 (4)	Ru1—N5	2.057 (5)
Cl1—Ru1—N1	93.7 (1)	N1—Ru1—N5	100.2 (2)
Cl1—Ru1—N2	172.6 (1)	N2—Ru1—N3	89.1 (2)
Cl1—Ru1—N3	90.5 (1)	N2—Ru1—N4	96.2 (2)
Cl1—Ru1—N4	91.0 (1)	N2—Ru1—N5	93.7 (2)
Cl1—Ru1—N5	89.2 (1)	N3—Ru1—N4	80.5 (2)
N1—Ru1—N2	79.1 (2)	N3—Ru1—N5	159.9 (2)
N1—Ru1—N3	99.8 (2)	N4—Ru1—N5	79.4 (2)
N1—Ru1—N4	175.3 (2)		

All H atoms were placed at calculated positions, with C—H distances of 0.95–0.99 Å, and with U_{iso}(H) = U_{eq}(C). The maximum difference-density peak is 2.61 Å from H21. In the crystal structure there are voids of 103 Å^3, which may accommodate water or acetonitrile solvent molecules. However, significant residual densities in the void could not be observed in the difference Fourier map.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 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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