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cis-(2,2′-Bipyridine)bis[2-(2-pyridyl)-4-methoxycarbonylquinoline]ruthenium(II) hexafluorophosphate

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The Ru atom of the title compound, $[Ru(C_{16}H_{12}N_2O_2)_2(C_{10}H_8N_2)](PF_6)_2$, is octahedrally coordinated to the N atoms of 2-(2-pyridyl)-4-methoxycarbonylquinoline and to those of a bipyridine ligand which are *cis* to each other. Owing to the rigidity of the 2-(2-pyridyl)-4-methoxycarbonylquinoline ligand, the complex is a distorted octahedron with Ru—N distances of 2.119 (2), 2.062 (2) and 2.043 (2) Å. Half a complex cation and one hexafluorophosphate counter-ion form the asymmetric unit. The complex cation lies on a twofold axis running along the line joining the Ru atom and the midpoint of the C17—C17($-x$, y, $\frac{1}{2} - z$) bond.

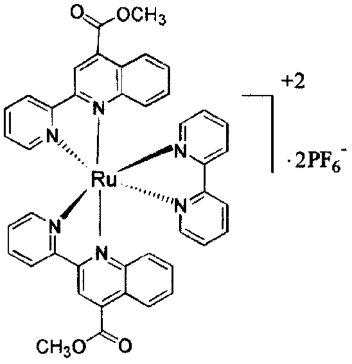
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.043
wR factor = 0.110
Data-to-parameter ratio = 14.5

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

Comment

In our continuing effort to synthesize and characterize multichromophore electroactive ruthenium(II)-containing polymeric systems, we have prepared novel ruthenium(II) complexes containing difunctional bipyridyl-like ligands. These complexes have been covalently attached into polymeric (Farah & Pietro, 1999, 2000, 2001; Farah *et al.*, 2000) and CdS nanocluster assemblies (Veinot *et al.*, 2000) through appropriate chemical modification. Detailed structural information is important in achieving a better understanding of the different photochemical, photophysical and electrochemical properties of the ruthenium chromophores (Juris *et al.*, 1988). In the light of these considerations, we describe here the synthesis and single-crystal structure of the title complex, (I) (Fig. 1).



(I)

This complex contains two functionalizable sites which make it an ideal synthon for the construction of polymetallic and transition-metal-containing dendrimers. The geometry of the dication is that of a distorted octahedron. When the four

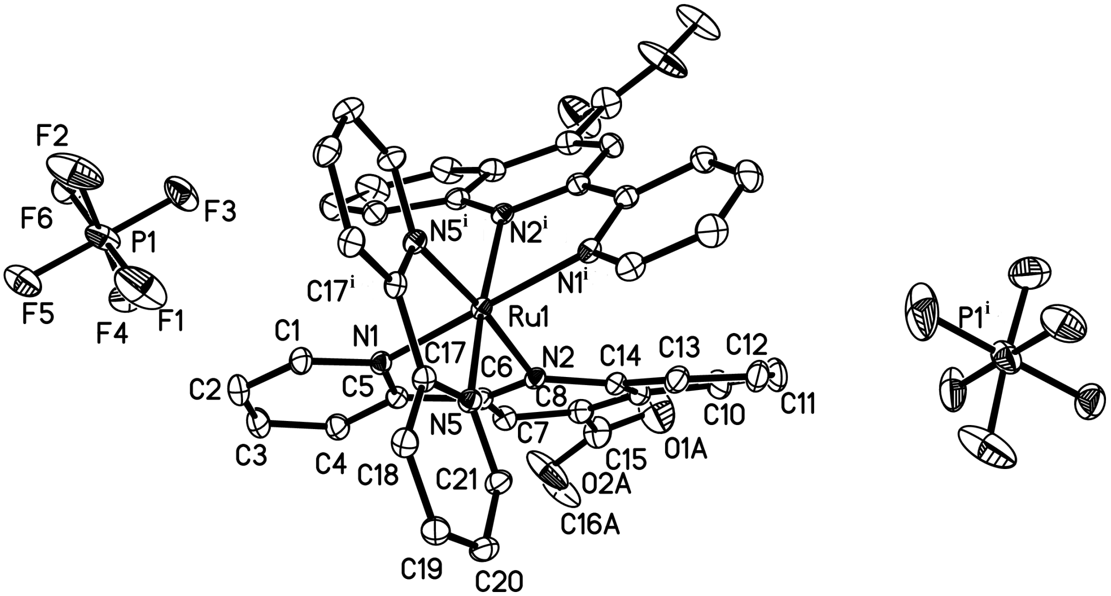


Figure 1
ORTEP drawing with atomic numbering of the title compound. Displacement ellipsoids are plotted at the 50% probability level. H atoms have been omitted for clarity.

atoms consisting of N2, N5 and their symmetry equivalents [N2^{i} and N5^{i}; symmetry code: (i) $-x, y, \frac{1}{2} - z$] are considered to make the plane (with *trans* N1 and N1^{i}), the average mean deviation from this plane is 0.1005 Å, with the Ru atom lying in it. The *trans* bond angle N1—Ru—N1^{i} is 175.62 (13)°. None of the equatorial *cis* angles is close to the idealized value of 90°. The N2—Ru—N2^{i} angle is found to be 81.42 (12)°, while the N5—Ru—N5^{i} angle is 78.81 (13)°. Alternatively, if a plane is considered to pass through N1, N1^{i}, N2 and N5^{i}, the Ru atom lies 0.0212 Å above it, the *trans* bond angle N5—Ru—N2^{i} is 174.35 (9)° and the two angles N1—Ru—N2 and N5^{i}—Ru—N1^{i} are 77.48 (9) and 86.50 (9)°, respectively. The steric interaction between the bulky 2-(2-pyridyl)-4-methoxycarbonylquinoline ligand and the bipyridine ligand results in an extension of the Ru—N2 distance in the quinoline moiety. This bond length of 2.119 (2) Å is longer than Ru—N1 as well as the value observed for Ru(bpy)$_3^{2+}$ (Ichida *et al.*, 1989). Consequently, the N1—Ru—N2 has the smallest bite angle of 77.48 (9)° to compensate for this effect. This finding may be related to the distorted structure of the complex and the different rigidity of the 2-(2-pyridyl)-4-methoxycarbonylquinoline ligand and the bipyridine. Similar distortions have been found in the solid state for polypyridyl ruthenium(II) complexes with rigid and sterically hindered ligands (Rillema *et al.*, 1979). The Ru—N distance in the bipyridine ligand is shortened [*versus* Ru(bpy)$_3^{2+}$] (Ichida *et al.*, 1989) to account for the withdrawn electron density.

Experimental

For the preparation of (I), dichloro-*cis*-bis[2(2-pyridyl)-4-methylcarboxyquinoline]ruthenium(II) (0.31 g, 0.43 mmol) was dissolved in 20 ml of methanol and 0.183 g (1.10 mmol) AgNO$_3$ was added to the dissolved substrate and the solution was left stirring for 2 h. The resulting white precipitate was then filtered off and 72 mg (0.45 mmol) of 2,2′-bipyridine in 10 ml of methanol was added to the filtrate which was then left to reflux for 24 h. The solvent was removed by rotary evaporation and the resulting dark-red product was purified by column chromatography (alumina) using methylene chloride/methanol (1:1, *v*/*v*) as the eluant. After concentrating the volume of the eluant to 30 ml, the product was precipitated with saturated aqueous potassium hexafluorophosphate. The resulting shiny dark-red product was then washed with ether and vacuum dried (yield: 0.35 g, 76%).

Crystal data

[Ru(C$_{16}$H$_{12}$N$_2$O$_2$)$_2$-(C$_{10}$H$_8$N$_2$)](PF$_6$)$_2$
M_r = 1075.75
Monoclinic, $C2/c$
a = 23.6702 (5) Å
b = 13.5602 (3) Å
c = 16.6057 (4) Å
β = 126.7172 (11)°
V = 4272.49 (17) Å^3
Z = 4

D_x = 1.672 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20509 reflections
θ = 2.6–27.5°
μ = 0.55 mm^{-1}
T = 150 (1) K
Prism, dark-red
0.35 × 0.13 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.832, $T_{\max}$ = 0.958
15 700 measured reflections
4797 independent reflections

4271 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024
$\theta_{\max}$ = 27.5°
$h = -30 \rightarrow 30$
$k = -17 \rightarrow 17$
$l = -21 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.110
S = 1.12
4797 reflections
330 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 12.6286P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 1.18 e Å^{-3}
$\Delta\rho_{\min}$ = −1.04 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Ru1—N5	2.043 (2)	N2—C6	1.341 (4)
Ru1—N1	2.062 (2)	N2—C14	1.387 (4)
Ru1—N2	2.119 (2)	N5—C21	1.342 (4)
N1—C1	1.353 (4)	N5—C17	1.360 (4)
N1—C5	1.358 (4)		
N5$^{\rm i}$—Ru1—N5	78.81 (13)	N1—Ru1—N2	77.48 (9)
N5$^{\rm i}$—Ru1—N1	96.89 (9)	N2—Ru1—N2$^{\rm i}$	81.42 (12)
N5—Ru1—N1	86.50 (9)	C1—N1—C5	118.1 (3)
N1$^{\rm i}$—Ru1—N1	175.62 (13)	C5—N1—Ru1	116.00 (18)
N5$^{\rm i}$—Ru1—N2	174.35 (9)	C6—N2—C14	117.7 (2)
N5—Ru1—N2	100.15 (9)	C14—N2—Ru1	127.13 (19)
N1$^{\rm i}$—Ru1—N2	99.14 (9)	C21—N5—Ru1	125.0 (2)

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

During the structure refinement, the atoms of the ester group (C15, O1, O2 and C16) all had very large anisotropic displacement parameters. There was an improvement in the refinement when these atoms were treated as disordered atoms. The final disorder model consists of two positions for the ester group rotationally disordered about the C8—C15 bond which each have 50% occupancy.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1999); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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