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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.033
 wR factor = 0.096
Data-to-parameter ratio = 16.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

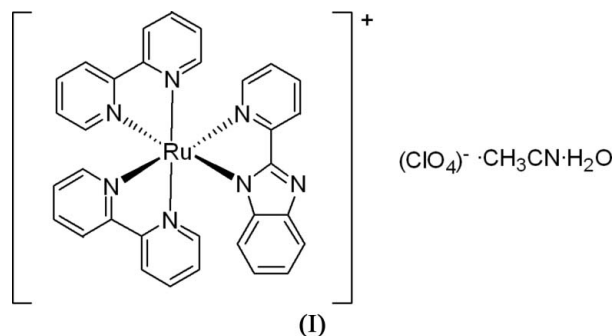
Bis(2,2'-bipyridine)[2-(2-pyridyl)-1H-benzimidazol-1-yl]ruthenium(II) perchlorate acetonitrile solvate monohydrate

The title complex, $[\text{Ru}(\text{C}_{12}\text{H}_8\text{N}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{ClO}_4 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$, was grown by diethyl ether diffusion into an acetonitrile solution from acetonitrile at room temperature. The Ru^{II} ion is in a distorted octahedral environment coordinated by two 2,2'-bipyridine (bpy) and one deprotonated 2-(2-pyridyl)benzimidazole (PIB) ligand. Charge is balanced by a perchlorate counter-ion. The free water molecule links an O atom of the perchlorate ion and the uncoordinated N atom of the ligand PIB by hydrogen bond.

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Comment

Ruthenium(II) complexes have been investigated extensively during the past two decades due to their rich photochemical and photophysical properties (Juris *et al.*, 1988). Apart from the studies on ruthenium complexes containing 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) ligands, many other ligand systems, such as biimidazole and its derivatives, have also been investigated (Juris *et al.*, 1988). Results indicate that the deprotonation of coordinated imidazoles provides a practicable means to tune the redox and photophysical properties of the complexes (Haga *et al.*, 1991).



However, a literature survey on deprotonated ruthenium(II) complexes showed that few crystal structures had been determined (Chao *et al.*, 2004). In an attempt to obtain more insight into the structural properties of such complexes, we present here the crystal structure of the title complex, $[\text{Ru}(\text{PIB})(\text{bpy})_2]\text{ClO}_4 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$, (I) [PIB = deprotonated 2-(2-pyridyl)benzimidazole]. The title complex consists of a $[\text{Ru}(\text{PIB})(\text{bpy})_2]^+$ cation, a disordered ClO_4^- anion, an acetonitrile molecule and a water molecule. As shown in Fig. 1, the central Ru atom is chelated by two bpy ligands and a PIB ligand. The coordination geometry about the Ru atom is distorted octahedral. The dihedral angles between the pyridine rings of the two bpy ligands of the complex are non-equivalent, one being $6.32(10)^\circ$ and the other $4.98(16)^\circ$;

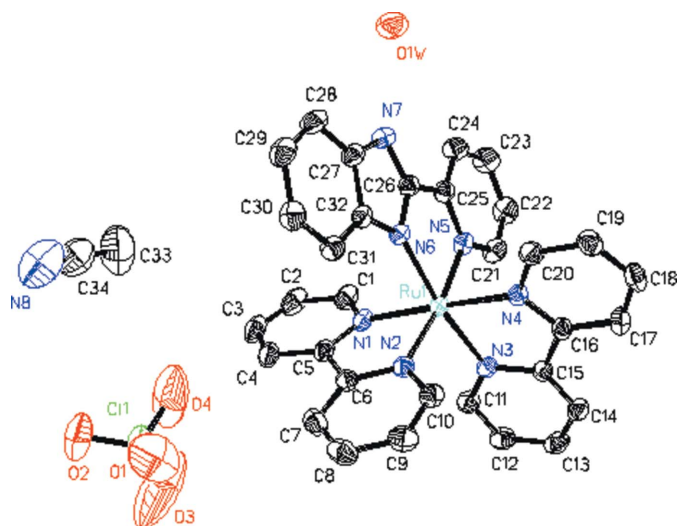


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted.

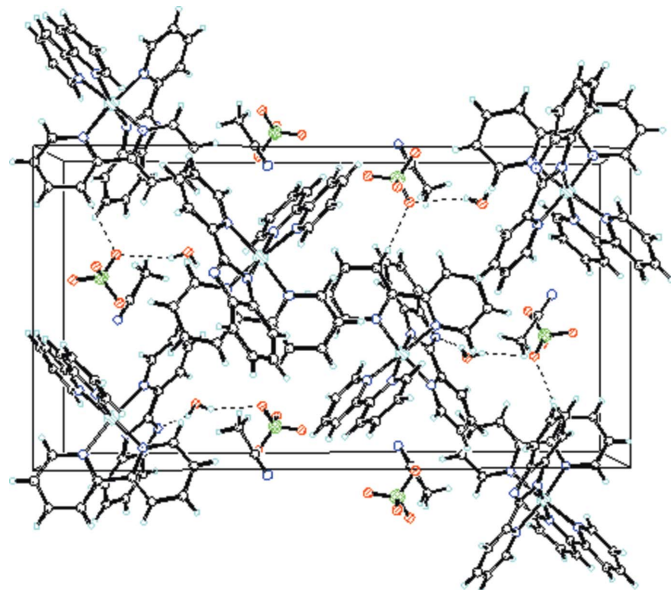


Figure 2
The crystal packing of the complex, viewed down the *a* axis, showing hydrogen bonds as dashed lines.

however, they are both in the range expected for this type of compound. The mean Ru–N bond length (2.061 Å) is comparable with those of published ruthenium(II) complexes.

Experimental

2-(2-Pyridyl)benzimidazole (PIBH; Walter *et al.*, 1954) and [Ru(PIBH)(bpy)₂](ClO₄)₂ (Haga, 1983) were synthesized by procedures reported in the literature. A solution of [Ru(PIBH)(bpy)₂](ClO₄)₂ (0.19 mmol, 0.15 g) in methanol was added to a sodium methoxide solution which was prepared *in situ* by dissolving sodium metal (0.72 mmol, 0.017 g) in methanol (10 ml). The color of the solution changed from red to dark red. The solution was heated with stirring for 30 min and then cooled to 273–278 K in a refrigerator. A

deep-red microcrystalline solid was collected by filtration. Deep-red single crystals of (I) suitable for an X-ray crystallographic study were grown by diethyl ether diffusion into an acetonitrile solution at room temperature. Calculated (%) for C₃₄H₂₉ClN₈O₅Ru: C 53.30, H 3.82, N 14.63; found (%): C 53.27, H 3.86, N 14.61.

Crystal data

[Ru(C₁₂H₈N₃)(C₁₀H₈N₂)₂]-
ClO₄·C₂H₃N·H₂O
M_r = 766.18
Monoclinic, *P*2₁/*c*
a = 9.5382 (16) Å
b = 13.749 (2) Å
c = 25.434 (4) Å
β = 93.214 (3)°
V = 3330.2 (9) Å³
Z = 4

D_x = 1.528 Mg m⁻³
Mo *Kα* radiation
Cell parameters from 724
reflections
θ = 1.7–27°
μ = 0.61 mm⁻¹
T = 293 (2) K
Block, red
0.50 × 0.30 × 0.26 mm

Data collection

Bruker SMART APEX CCD area-
detector diffractometer
φ and *ω* scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
T_{min} = 0.752, *T_{max}* = 0.858
21799 measured reflections

7254 independent reflections
6251 reflections with *I* > 2σ(*I*)
R_{int} = 0.017
θ_{max} = 27.0°
h = -12 → 9
k = -17 → 16
l = -29 → 32

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.096
S = 1.02
7254 reflections
451 parameters
H atoms treated by a mixture of
independent and constrained
refinement

w = 1/[σ²(*F_o*²) + (0.0555*P*)²
+ 1.9135*P*]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/σ)_{max} = 0.002
Δρ_{max} = 0.88 e Å⁻³
Δρ_{min} = -0.56 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Ru1–N2	2.040 (2)	Ru1–N1	2.059 (2)
Ru1–N4	2.0524 (19)	Ru1–N6	2.0680 (19)
Ru1–N3	2.0554 (19)	Ru1–N5	2.083 (2)
N2–Ru1–N4	98.07 (8)	N3–Ru1–N6	171.51 (8)
N2–Ru1–N3	90.33 (8)	N1–Ru1–N6	85.44 (8)
N4–Ru1–N3	78.76 (8)	N2–Ru1–N5	172.88 (8)
N2–Ru1–N1	78.77 (8)	N4–Ru1–N5	87.44 (8)
N4–Ru1–N1	176.82 (8)	N3–Ru1–N5	95.19 (8)
N3–Ru1–N1	100.84 (8)	N1–Ru1–N5	95.74 (8)
N2–Ru1–N6	96.54 (8)	N6–Ru1–N5	78.37 (8)
N4–Ru1–N6	95.29 (8)		

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1W–H1WA...O4 ⁱ	0.74 (5)	2.47 (5)	3.153 (8)	155 (4)
O1W–H1WB...N7	0.98 (9)	1.92 (9)	2.826 (4)	153 (6)

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

All H atoms were positioned geometrically and refined as riding, with isotropic displacement parameters 1.3 to 1.7 times the *U_{eq}* value of the parent atom. The C–H distances are in the range 0.93–0.96 Å. Water H atoms were refined freely. Possible perchlorate disorder could not be satisfactorily modeled.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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