Crystal Structure of the [Ru(azpy)₂(bpy)](PF₆)₂ Complex (azpy = 2-(phenylazo)pyridine, bpy = 2,2'-bipyridine)

Kanidtha HANSONGNERN,^{*†} Uraiwan CHANGSALUK,^{*} Jian-Sung WU,^{**} and Tian-Huey LU^{**}

^{*}Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

^{**}Department of Physics, National Tsing Hua University, Hsinchu, 300, Taiwan

The complex [Ru(azpy)₂(bpy)](PF₆)₂ (azpy=2-(phenylazo)pyridine, bpy=2,2'-bipyridine) was synthesized and characterized by X-ray diffraction analysis. The coordination geometry around ruthenium(II) was distorted octahedral with coordinating from two *N*-donor centers of bpy and four *N*-donor centers of two azpy units. The Ru-N (pyridine of azpy) distance was (average, 2.048(4) Å), shorter than the Ru-N (bpy) distance (average, 2.088(4) Å). The average N=N distance in the title compound was 1.278(5) Å, slightly longer than that of the free azpy ligand, 1.248(4) Å. These results confirm that azpy is a stronger π -acceptor than bpy.

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Since the discovery of antitumor activity of cisplatin (*cis*-diamminedichloroplatinum(II), *cis*-[PtCl₂(NH₃)₂], many other metal complexes have been investigated for their possible applications as antitumor drugs. At present, several ruthenium complexes are known for their cytotoxic or antitumor activities. For example, the isomers of [Ru(azpy)₂Cl₂], (where azpy=2-(phenylazo)pyridine) were found to be reactive as anticancer agents, especially the *ctc*-[Ru(azpy)₂Cl₂] complex (*ctc*-indicating the coordinating chlorides, the pyridine nitrogens and the azo nitrogens in mutual *cis*, *trans*, and *cis* orientation) or α -[Ru(azpy)₂Cl₂]. This isomer has shown a remarkably high *in vitro* cytotoxicity in many cell lines, such as MCF-7 (breast cancer), IGROV (ovarian cancer) and H226 (nonsmall cell lung cancer).¹ The water-soluble compound α -[Ru(azpy)₂(NO₃)₂] was also prepared, and its binding to the (DNA-model) bases 9-ethylguanine and guanosine was studied.² In this work, it is our interest to study the structure of the ruthenium(II) complex, [Ru(azpy)₂bpy](PF₆)₂ and to relate to its anticancer activity later on.

The α -[Ru(azpy)₂Cl₂] complex was synthesized by a procedure reported in the literature.³ A mixture of α -[Ru(azpy)₂Cl₂] 0.40 mmol, AgNO₃ 0.83 mmol, and bpy 0.40

mmol was dissolved in 60 mL of ethanol. The purple solution was refluxed for 12 h, resulting in a red-brown solution. After cooling to room temperature, the solution was filtered to remove AgCl. Then, a solution of NH₄PF₆ was added to the filtrate. After 2 days, the solid was collected and crystals suitable for X-ray techniques were selected from the obtained solid. Details of the X-ray structure determination of the title compound are given in Tables 1 and 2.

The ruthenium center is in a distorted octahedral environment

Table 1 Crystal and experimental data

Empirical formula: C ₃₂ H ₂₆ N ₈ P ₂ F ₁₂ Ru
Formula weight = 913.62
Crystal system: orthorhombic <i>Z</i> = 8
Space group: <i>Pbca</i>
Temperature = 297 K
Radiation: Mo <i>K</i> α (λ = 0.71073 Å)
μ (Mo <i>K</i> α) = 0.597 mm ⁻¹
Crystal size: 0.30 × 0.20 × 0.20 mm
<i>a</i> = 19.4937(11) Å
<i>b</i> = 16.3842(10) Å
<i>c</i> = 23.5940(14) Å
<i>V</i> = 7535.7(8) Å ³
Density (calculated): 1.611 Mg/m ³
<i>F</i> (0 0 0) = 3648
Goodness-of-fit on <i>F</i> ² 1.019
Color: red
2 θ _{max} = 56.5°
(Δ / σ) _{max} = 0.000
($\Delta\rho$) _{max} = 0.744 e Å ⁻³
($\Delta\rho$) _{min} = -0.345 e Å ⁻³
<i>R</i> = 0.0429; <i>wR</i> = 0.1111
Measurement: Bruker SMART CCD
Structure determination: Patterson method (SHELXS97)
Refinement: full-matrix on <i>F</i> ² (SHELXS97)
Molecular graphics: ORTEP32
CCDC deposit number: 627567

Fig. 1 Structural chemical diagram.

[†] To whom correspondence should be addressed.
E-mail: kanidtha.h@psu.ac.th or kanidthah@yahoo.com

Fig. 2 Molecular structure of $[\text{Ru}(\text{azpy})_2(\text{bpy})](\text{PF}_6)_2$ with the atom numbering scheme.

Table 2 Selected bond lengths [Å] and angles [°] of $[\text{Ru}(\text{azpy})_2(\text{bpy})](\text{PF}_6)_2$

Ru-N4	2.009(4)	Ru-N6	2.041(4)
Ru-N3	2.044(4)	Ru-N1	2.055(4)
Ru-N7	2.082(4)	Ru-N8	2.094(4)
N1-C1	1.335(6)	N1-C5	1.359(6)
N3-N2	1.285(5)	N3-C22	1.428(6)
N8-C16	1.335(6)	N8-C12	1.363(6)
N4-N5	1.271(5)	N4-C6	1.439(6)
N6-C32	1.342(6)	N6-C28	1.356(7)
N7-C17	1.337(6)	N7-C21	1.360(6)
N2-C5	1.393(6)	N5-C28	1.407(7)
N4-Ru-N6	76.80(17)	N4-Ru-N3	83.35(15)
N6-Ru-N3	98.23(17)	N4-Ru-N1	96.36(16)
N6-Ru-N1	171.52(16)	N3-Ru-N1	75.77(16)
N4-Ru-N7	97.29(16)	N6-Ru-N7	86.15(16)
N3-Ru-N7	175.59(16)	N1-Ru-N7	99.82(16)
N4-Ru-N8	172.88(16)	N6-Ru-N8	97.71(16)
N3-Ru-N8	102.09(16)	N1-Ru-N8	89.49(15)
N7-Ru-N8	77.64(17)		

with four nitrogens (N1, N3, N4, N6) of two azpy ligands and the two nitrogens (N7, N8) of one bpy ligand. The pyridine rings of azpy are at the trans position and the two pyridine rings of bpy ligand are trans to the azo groups of the azpy ligands. The *trans*-angles around the ruthenium center in the plane range

from $171.5(16)^\circ$ to $175.6(16)^\circ$, indicating distortions from the rectilinear geometry. The bite angles extended by two azpys and one bpy are $75.7(16)^\circ$, $76.8(17)^\circ$ and $77.6(17)^\circ$, respectively. The average bond distance of Ru-N (azo), $2.027(4)\text{Å}$ is shorter than the average Ru-N (pyridine of azpy) bond length of $2.048(4)\text{Å}$. This is due to greater π -backbonding, from $d\pi(\text{Ru}) \rightarrow \pi^*(\text{azo})$. In addition, it is noted that the Ru-N (bpy) distance (average, $2.088(4)\text{Å}$) is longer than those in $[\text{Ru}(\text{bpy})_3]^{2+}$ (average, $2.056(6)\text{Å}$).⁴ This is probably due to the competition for the electron density from the metal ion between the azpy and bpy ligands. Moreover, in the title complex the average N=N distance of azpy is $1.278(5)\text{Å}$ which is slightly longer than that of the free azpy (N=N $1.248(4)\text{Å}$).⁵ The coordination of azpy leads to a decrease in the N=N bond order due to the σ -donor and the π -acceptor character of the ligand. The results from the molecular structure of the title compound confirm that azpy is a better π -acceptor than bpy.

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