

**(Nitro- $\kappa N$ )[2-(phenyldiazenyl- $\kappa N^2$ )-pyridine- $\kappa N$ ](2,2':6',2''-terpyridine- $\kappa^3 N$ )ruthenium(II) tetrafluoroborate<sup>1</sup>**Kanidtha Hansongnern,<sup>a</sup> Uraivan Saeteaw,<sup>a</sup> Jack Cheng,<sup>b</sup> Fen-Ling Liao<sup>c</sup> and Tian-Huey Lu<sup>b\*</sup><sup>a</sup>Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkla 90112, Thailand, <sup>b</sup>Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Taiwan, and <sup>c</sup>Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

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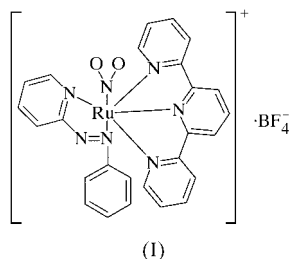
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The Ru—N bond distances in the title complex,  $[\text{Ru}(\text{NO}_2)(\text{C}_{11}\text{H}_9\text{N}_3)(\text{C}_{15}\text{H}_{11}\text{N}_3)]\text{BF}_4$  or  $[\text{Ru}(\text{NO}_2)(\text{tpy})(\text{azpy})]\text{BF}_4$ , [tpy is 2,2':6',2''-terpyridine and azpy is 2-(phenylazo)-pyridine], are Ru—N<sub>py</sub> 2.063 (4), Ru—N<sub>azo</sub> 2.036 (4), Ru—N<sub>nitro</sub> 2.066 (3) Å, and Ru—N<sub>tpy</sub> 2.082 (4), 1.982 (3) and 2.074 (4) Å. The azo N atom is *trans* to the nitro group. The azo N=N bond length is 1.265 (5) Å, which is the shortest found in such complexes to date. This indicates a multiple bond between Ru and the N atom of the nitro group, and  $\pi$ -backbonding [ $d\pi(\text{Ru}) \rightarrow \pi^*(\text{azo})$ ] is decreased.

**Comment**

Complexes of ruthenium(II) with polypyridine ligands, such as 2,2':6',2''-terpyridine (tpy) and bidentate ligands, have been extensively studied. One reason for this is that they could lead to high-valence ruthenium-oxo complexes, which act as catalysts in the oxidation of carbohydrates. Thorp and co-workers have demonstrated that the oxoruthenium(IV) complex  $[\text{Ru}^{\text{IV}}(\text{tpy})(\text{bpy})\text{O}^{2+}]$  (bpy is 2,2'-bipyridine) is an efficient DNA cleavage reagent (Grover *et al.*, 1992). The interesting properties of the class  $[\text{Ru}(\text{tpy})(\text{bpy})\text{X}]^{n+}$ , where X



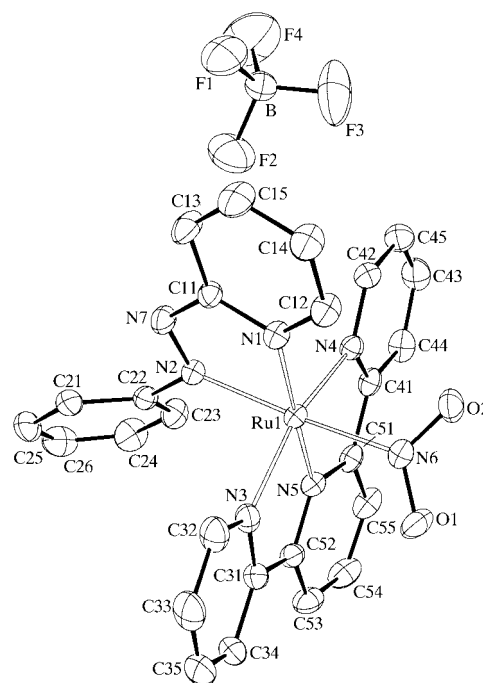
is monodentate, led us to synthesize ruthenium complexes with other bidentate ligands which are better  $\pi$ -acceptors than bpy, such as 2-(phenylazo)pyridine (azpy; Krause & Krause,

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1980), in order to extend the variety of such compounds and to probe the nature of bonding in such complexes. In this report, we describe the synthesis and the crystal and molecular structures of the title complex,  $[\text{Ru}(\text{NO}_2)(\text{tpy})(\text{azpy})]\text{BF}_4$ , (I). The aim of studying this compound is to explore how the co-ligand,  $\text{NO}_2^-$ , affects the bonding in the complex molecule.

The coordination geometry around the Ru atom in (I) is distorted octahedral. The equatorial positions are occupied by three pyridine N atoms from the tpy ligand and one pyridine N atom from the azpy molecule. In this complex, the nitrite ligand is bound to Ru through the N atom, which is *trans* to the azo nitrogen from azpy.

As expected, the Ru—N bond to the central pyridyl ring of the terpyridine ligand [Ru1—N5 1.982 (3) Å] is the shortest bond, whereas the terminal Ru1—N3 [2.082 (4) Å] and Ru1—N4 [2.074 (4) Å] bonds are lengthened, to relieve strain and retain a typical terpyridine bite angle of 79°. This situation is similar to that found in other ruthenium complexes containing terpyridine ligands (Leising *et al.*, 1990; Gerli *et al.*, 1995; Gulyas *et al.*, 1996). The Ru1—N1 (pyridine in azpy) distance of 2.063 (4) Å is longer than the Ru1—N2 (azo) distance of 2.036 (4) Å. This indicates that there is a strong interaction between Ru and N<sub>azo</sub> as  $\pi$ -backbonding. Meanwhile, the azo N2 atom *trans* to N6 from the nitro group gives rise to an interesting result. The Ru1—N6 (nitro) bond distance of 2.066 (3) Å found in (I) is significantly shorter than those reported for other (nitro)ruthenium(II) complexes, for example, 2.074 (6) Å in *trans*- $[\text{Ru}(\text{tpy})(\text{NO}_2)(\text{PMe}_3)_2]\text{ClO}_4$  (Leising *et al.*, 1990). This could be due to some Ru—N<sub>nitro</sub> multiple bonding in (I). On the other hand, the Ru1—N2 (azo) bond [2.036 (4) Å] is longer than the values found in other

**Figure 1**

The molecular structure of (I) showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

ruthenium–azpy complexes, such as 1.977 (4) and 1.984 (4) Å in [Ru(azpy)<sub>2</sub>Cl<sub>2</sub>] (Seal & Ray, 1984), and 1.971 (7) Å in [Ru(tpy)(azpy)(CH<sub>3</sub>CN)]<sup>2+</sup> (Pramanik *et al.*, 1998).

In addition, the observed variation of the N=N bond lengths is indicative of  $\pi$ -backbonding between Ru and the N<sub>azo</sub> atom. In the complex ion of (I), the N=N bond distance is 1.265 (5) Å, which is shorter than the values observed in other complexes (Seal & Ray, 1984; Pramanik *et al.*, 1998) and close to the value found in the uncoordinated azpy ligand [1.248 (4) Å; Panneerselvam *et al.*, 2000]. The lengthening of the Ru1–N2(azo) distance suggests less Ru–N  $\pi$  interaction at this centre, possibly due to a greater Ru–NO<sub>2</sub>  $\pi$  interaction. This confirms that the nitro group also has considerable  $\pi$  interactions with the Ru centre, as seen clearly from this complex. Therefore, the N=N bond length can be a useful probe for the relative strength of the Ru–N(azo) bond.

## Experimental

Commercial ruthenium trichloride was purchased from Aldrich and 2,2':6'2''-terpyridine was obtained from Fluka. [Ru(tpy)Cl<sub>3</sub>] and 2-(phenylazo)pyridine were synthesized according to the methods of Sullivan *et al.* (1980) and Campbell *et al.* (1953). [Ru(tpy)(azpy)Cl]Cl was synthesized using a modification of the procedure published by Takeuchi *et al.* (1984). The synthesis of [Ru(NO<sub>2</sub>)(tpy)(azpy)]BF<sub>4</sub> (I), was as follows: [Ru(tpy)(azpy)Cl]Cl (52 mg) and silver nitrate (30 mg) were heated at reflux in an acetone–water solution (12 ml; 3:1 v/v). The resulting silver chloride was filtered off and the filtrate was heated for 15 min and NaNO<sub>2</sub> (40 mg) added. The reaction mixture was heated for a further 1 h and then NH<sub>4</sub>BF<sub>4</sub> (45 mg) was added. After standing for 5 d, the solid was filtered off and washed with cool water and diethyl ether (yield 88%). Crystals of (I) suitable for X-ray analysis were recrystallized from a solution in a mixture of methanol and acetone (1:1 v/v).

### Crystal data

[Ru(NO <sub>2</sub> )(C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> )- (C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> )]BF <sub>4</sub>	$D_x = 1.665 \text{ Mg m}^{-3}$
$M_r = 650.37$	Mo $K\alpha$ radiation
Monoclinic, $Pc$	Cell parameters from 8214 reflections
$a = 9.2347 (13) \text{ \AA}$	$\theta = 2.1\text{--}28.3^\circ$
$b = 9.6814 (13) \text{ \AA}$	$\mu = 0.67 \text{ mm}^{-1}$
$c = 14.588 (2) \text{ \AA}$	$T = 296 (2) \text{ K}$
$\beta = 95.948 (2)^\circ$	Needle, black
$V = 1297.2 (3) \text{ \AA}^3$	$0.3 \times 0.3 \times 0.2 \text{ mm}$
$Z = 2$	

### Data collection

Siemens SMART CCD area-detector diffractometer	3233 independent reflections (plus 1494 Friedel-related reflections)
Oscillation scans	4484 reflections with $I > 2\sigma(I)$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.788$ , $T_{\text{max}} = 0.916$	$\theta_{\text{max}} = 28.3^\circ$
7966 measured reflections	$h = -10 \rightarrow 12$
	$k = -12 \rightarrow 12$
	$l = -18 \rightarrow 18$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$
4727 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
370 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = $-0.06 (2)$

**Table 1**  
Selected geometric parameters (Å, °).

Ru1–N5	1.982 (3)	Ru1–N3	2.082 (4)
Ru1–N2	2.036 (4)	B–F3	1.334 (6)
Ru1–N1	2.063 (4)	B–F2	1.342 (5)
Ru1–N6	2.066 (3)	B–F1	1.362 (6)
Ru1–N4	2.074 (4)	B–F4	1.367 (8)
N5–Ru1–N2	103.04 (13)	N1–Ru1–N4	97.26 (15)
N5–Ru1–N1	176.31 (17)	N6–Ru1–N4	87.86 (12)
N2–Ru1–N1	75.57 (13)	N5–Ru1–N3	79.03 (15)
N5–Ru1–N6	85.04 (15)	N2–Ru1–N3	92.53 (14)
N2–Ru1–N6	171.88 (14)	N1–Ru1–N3	104.37 (15)
N1–Ru1–N6	96.40 (13)	N6–Ru1–N3	88.24 (14)
N5–Ru1–N4	79.38 (14)	N4–Ru1–N3	158.31 (11)
N2–Ru1–N4	94.32 (13)		

H atoms were placed with geometrical constraints (C–H = 0.93 Å) and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SHELXTL (Bruker, 1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: NRCVAX (Gabe *et al.*, 1989); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1141). Services for accessing these data are described at the back of the journal.

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