Crystal Structure of Bromo(2,2':6',2''-terpyridine)(2-(phenylazo)-pyridine)ruthenium(II) Tetrafluoroborate

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The title compound, $C_{26}H_{20}N_6BrRu(BF_4)$, crystallizes in the centrosymmetric space group $P2_1/n$ and consists of discrete complex units. The Ru(II) ion is octahedrally coordinated to one 2,2':6',2''-terpyridine (tpy), one 2-(phenylazo)pyridine (azpy) and a Br atom in *trans*-axial position at a distance of 2.547(5) Å. The shorter Ru-N (azo) distance (1.960(3) Å) than the Ru-N(py) distance (2.061(3) Å) signifies a strong π -backbonding, which leads to a longer, N=N (azo) bond (1.304(4) Å).

The polypyridine complexes of a type $[Ru(tpy)(L)X]^{n+}$ (where tpy = 2,2':6',2''-terpyridine, L = a bidentate ligand such as 2,2'-bipyridine (bpy), X = a monodentate ligand and $n = 0$ or 1) have generated considerable interest in several areas, for example, used as effective DNA cleavage agents¹ and as catalysts in oxidation of water to dioxygen² based on the corresponding high-valent ruthenium oxo complexes. It is our continuing interest to study structures of ruthenium(II) complexes with a bidentate ligand such as 2-(phenylazo)pyridine (azpy) according to its property as a strong π -acceptor.³

Azpy and $[Ru(tpy)Cl_3]$ were synthesized by procedures reported in the literatures.^{3,4} $[Ru(tpy)(azpy)Cl]Cl$ was prepared using a similar method to that described before.⁵ $[Ru(tpy)(azpy)Cl]Cl$ (52 mg) and $AgNO_3$ (30 mg) were refluxed in the mixture of acetone and water for 1 h and the solution was filtered while hot. LiBr (42 mg) was added to the filtrate, and the mixture was heated and refluxed for 1 h. NH_4BF_4 (45 mg) was added to the solution. After 5 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 1–3.

The ruthenium center is in a distorted octahedral environment with three nitrogens (N4, N5, N6) of the tpy ligand and the N1 (py) atom of azpy ligand in the equatorial plane. The *trans* axial positions are occupied by the N3 (azo) atom of azpy and the Br atom. The bite angle of azpy ligand (76.17(13)°) is

common in the azpy complexes.^{2,5} The mean Ru–N distance to the tpy ligand (2.042 Å) is similar to those found in $[Ru(tpy)(azpy)Cl]Cl$ (2.046 Å),⁵ $[Ru(tpy)(azpy)CH_3CN](ClO_4)_2$ (2.049 Å)² and $[Ru(tpy)(azpy)(NO_2)](BF_4)$ (2.046 Å).⁶ However, these are longer than those observed in the bpy complexes, for example, $[Ru(tpy)(bpy)(I)](PF_6)_2 \cdot 0.5C_7H_8$ (2.019 Å),⁷ $[Ru(tpy)(bpy)(pz)](PF_6)_2$ (2.013 Å),⁸ $[Ru(tpy)(bpy)-(CH_3CN)](PF_6)_2$ (2.031 Å),⁹ and $[Ru(tpy)(bpz)(Cl)](PF_6)_2 \cdot CH_3CN$ (2.037 Å).¹⁰ This phenomenon can be ascribed to the π -interaction between metal ion and ligands. Since azpy is a stronger π -acceptor than bpy and bpz, the ruthenium ion becomes an electron-rich center and lengthens the distances to tpy ligand in order to stabilize the structure of complex ion. The Ru–Br bond length in the title compound (2.547(5) Å) is slightly longer than those observed in $[Ru(C_5H_5)(CO)_2Br]$ (2.536(2) Å)¹¹ but shorter than those in $[Ru(Br)_2(Me_2SO)_4]$ (2.601(1), 2.578(1) Å).¹² The Ru–N(azo) distance (1.960(3) Å) is shorter than the Ru–N(py) distance (2.061(3) Å) and becomes shortest among the related complexes.^{2,5,6} This indicates that there is strong π -backbonding in the title compound, greater

Fig. 1 Structural chemical diagram.

Fig. 2 The molecular structure of $[Ru(tpy)(azpy)Br]BF_4$ with atom numbering scheme; displacement ellipsoids are drawn at 50% probability level.

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Table 1 Crystal and experimental data

Empirical formula: C ₂₆ H ₂₀ BBR ₄ N ₆ Ru
Formula weight = 684.27
Temperature = 293(2)K
Wavelength = 0.71073 Å
Crystal system: monoclinic
Space group: P2 ₁ /n Z = 4
Crystal size: 0.33 × 0.16 × 0.06 mm
a = 8.6395(5) Å
b = 15.9247(9) Å
c = 19.6620(11) Å
β = 100.5100(10)°
V = 2659.7(3) Å ³
D _x = 1.709 Mg/m ³
μ (Mo Kα) = 2.148 mm ⁻¹
F(0 0 0) = 1352
θrange = 1.66 – 28.28°, –11 < h < 10, –21 < k < 21; –26 < l < 24
Collected reflections = 17041
Unique reflections = 6379 [R _{int} = 0.0412]
Goodness-of-fit = 1.069
R = 0.0557; wR = 0.0947
(Δρ) _{max} = 0.562; (Δρ) _{min} = –0.617 e Å ⁻³
Measurement: Bruker SMART CCD
Structure determination: Patterson method (SHELXS97)
Refinement method: Full-matrix on F ² (SHELXL97)
Molecular graphics: ORTEP32

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å² × 10³)

Atom	x	y	z	U _{eq} ^a
Ru	0.94907(4)	0.10089(2)	0.191640(10)	32.08(12)
Br	0.82480(5)	-0.04100(3)	0.15540(2)	47.11(17)
N(1)	1.0452(4)	0.0658(2)	0.2913(2)	37.6(11)
N(2)	1.1254(4)	0.2072(2)	0.2966(2)	44.8(12)
N(3)	1.0470(4)	0.2042(2)	0.2334(2)	34.2(11)
N(4)	0.7336(4)	0.1502(2)	0.2034(2)	38.6(11)
N(5)	0.8669(4)	0.1389(2)	0.0961(2)	39.9(11)
N(6)	1.1332(4)	0.0669(2)	0.1426(2)	41.3(11)
C(1)	1.0367(5)	-0.0081(3)	0.3233(2)	51.9(17)
C(2)	1.1128(7)	-0.0219(3)	0.3903(3)	73(2)
C(3)	1.1982(8)	0.0412(4)	0.4265(3)	84(2)
C(4)	1.2109(6)	0.1164(3)	0.3949(2)	62.2(19)
C(5)	1.1262(5)	0.1284(3)	0.3278(2)	45.4(16)
C(6)	1.0177(5)	0.2871(2)	0.2020(2)	37.8(12)
C(7)	0.9393(5)	0.3460(3)	0.2347(2)	50.6(16)
C(8)	0.9003(7)	0.4213(3)	0.2017(3)	67(2)
C(9)	0.9397(6)	0.4375(3)	0.1386(3)	66(2)
C(10)	1.0141(6)	0.3778(3)	0.1064(2)	56.4(17)
C(11)	1.0539(5)	0.3014(2)	0.1377(2)	41.1(14)
C(12)	0.6775(5)	0.1594(3)	0.2615(2)	46.9(17)
C(13)	0.5442(6)	0.2051(3)	0.2663(3)	64.8(19)
C(14)	0.4622(6)	0.2409(4)	0.2072(3)	75(2)
C(15)	0.5155(6)	0.2301(3)	0.1447(3)	61.6(19)
C(16)	0.6512(5)	0.1850(3)	0.1440(2)	45.0(16)
C(17)	0.7221(5)	0.1730(3)	0.0822(2)	46.1(14)
C(18)	0.6542(6)	0.1924(3)	0.0139(2)	59.1(17)
C(19)	0.7424(8)	0.1749(3)	-0.0365(2)	75(2)
C(20)	0.8912(7)	0.1416(3)	-0.0215(2)	64(2)
C(21)	0.9518(6)	0.1237(3)	0.0466(2)	51.0(16)
C(22)	1.1072(6)	0.0860(2)	0.0743(2)	46.0(16)
C(23)	1.2271(7)	0.0720(3)	0.0355(3)	68(2)
C(24)	1.3676(7)	0.0384(3)	0.0674(3)	70(2)
C(25)	1.3908(6)	0.0154(3)	0.1355(3)	68(2)
C(26)	1.2697(6)	0.0307(3)	0.1713(3)	55.6(17)
B	0.2398(8)	0.3136(4)	-0.0481(3)	61(2)
F(1)	0.2745(5)	0.2946(3)	0.0192(2)	128(2)
F(2)	0.3166(6)	0.2661(4)	-0.0871(2)	169(3)
F(3)	0.0909(9)	0.2777(5)	-0.0683(4)	152(4) ^b
F(4)	0.2316(12)	0.3915(4)	-0.0622(4)	159(4) ^b
F(3A)	0.1054(11)	0.3461(7)	-0.0701(5)	136(5) ^c
F(4A)	0.3493(16)	0.3647(9)	-0.0483(9)	211(9) ^c

a. U_{eq} = (1/3)ΣΣU_{ij}a_i*a_j*(a_ia_j). b. s.o.f. 0.6. c. s.o.f. 0.4.

than in other complexes, and that bromide has a weaker π-bond interaction with the metal ion compared to chloride, acetonitrile and the nitro group. In addition, the N=N bond distance (1.304(4) Å), which is sensitive to the extent of π-backbonding in azpy ligand, is longer than those found in the other

Table 3 Selected bond lengths [Å] and angles [°]

Ru-N(3)	1.960(3)	Ru-N(5)	1.978(3)
Ru-N(1)	2.061(3)	Ru-N(4)	2.071(3)
Ru-N(6)	2.077(3)	Ru-Br	2.5469(5)
N(1)-C(1)	1.343(5)	N(1)-C(5)	1.347(5)
N(2)-N(3)	1.304(4)	N(2)-C(5)	1.397(5)
N(3)-C(6)	1.460(5)	N(4)-C(12)	1.327(5)
N(4)-C(16)	1.370(5)	N(5)-C(21)	1.344(5)
N(5)-C(17)	1.345(5)	N(6)-C(26)	1.341(5)
N(6)-C(22)	1.355(5)		
N(3)-Ru-N(5)	101.15(13)	N(3)-Ru-N(1)	76.17(13)
N(5)-Ru-N(1)	176.78(13)	N(3)-Ru-N(4)	87.89(12)
N(5)-Ru-N(4)	79.39(14)	N(1)-Ru-N(4)	102.16(12)
N(3)-Ru-N(6)	96.02(12)	N(5)-Ru-N(6)	79.13(14)
N(1)-Ru-N(6)	99.28(13)	N(4)-Ru-N(6)	158.52(13)
N(3)-Ru-Br	171.65(9)	N(5)-Ru-Br	86.90(9)
N(1)-Ru-Br	95.84(10)	N(4)-Ru-Br	91.49(9)
N(6)-Ru-Br	87.59(9)		

complexes.^{2,5,6}

During refinement, the F3 and F4 atoms of tetrafluoroborate anion were found to be distributed over two positions, F3, F4 and F3A, F4A, with site occupancy ratios 0.6/0.4. Hydrogen atoms were constrained to ride on the respective carbon (C-H 0.93 Å) with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom.

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