

# Binuclear *trans*- $\mu$ -pyrazine-bis[bromo-tetrapyridineruthenium(II)] dihexafluorophosphate dimethylformamide disolvate

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$

Some non-H atoms missing

Disorder in solvent or counterion

$R$  factor = 0.042

wR factor = 0.115

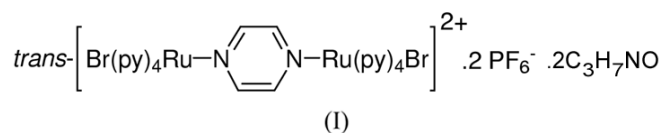
Data-to-parameter ratio = 19.8

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

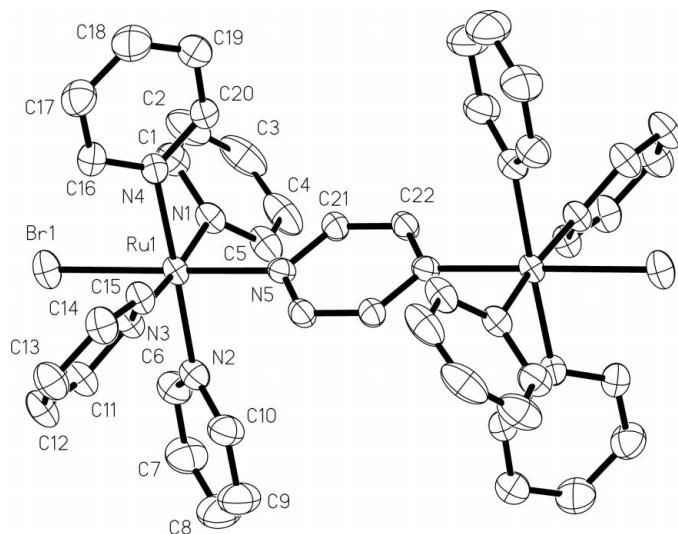
The Ru atoms of the title compound,  $[\text{Ru}_2\text{Br}_2(\text{C}_4\text{H}_4\text{N}_2)(\text{C}_5\text{H}_5\text{N})_8](\text{PF}_6)_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$ , are coordinated by the four N atoms of the pyridine (py) ligands and a bromide. Two such units are bridged by a pyrazine (pz) unit, which is disposed about a centre of inversion, so as to form a *trans* pseudo-octahedral geometry about Ru. The py units are in an eclipsed conformation when viewed down the internuclear axis. The Ru–N(pz) distance is 2.079 (3) Å, while the Ru–Br distance is 2.5524 (4) Å.

## Comment

In proceeding towards the synthesis of asymmetric binuclear complexes containing a chromophore on one terminus and a labile group on the other terminus, we have prepared several binuclear and trinuclear complexes using our synthon-based approach (Mirza & Lever, 2003). We describe here the synthesis and a single-crystal X-ray structure of the title complex, (I), that features a centrosymmetric dication, two  $\text{PF}_6^-$  anions and two DMF solvent molecules of crystallization.



The analysis revealed that the bond distance of Ru–N(pz), 2.079 (3) Å, is significantly longer than the corresponding Ru–N(pz) separations in the Creutz–Taube ion,  $[(\text{NH}_3)_5\text{Ru}]_2(\mu\text{-pz})^{4+}$  (Creutz & Taube, 1969; Fürholz *et al.*, 1985), which fall in the range 1.972 (4)–2.002 (2) Å, and essentially the same as in the recently reported  $[(\text{Cyclen})_4\text{Ru}_4(\mu\text{-pz})_4]^{9+}$  ion, at 2.020 (13) and 2.049 (12) Å (Lau *et al.*, 2002). These distances are slightly shorter than the average Ru–N(py) distance of 2.103 (3) Å calculated for (I), but similar to those in the analogous *trans*- $[\{\text{RuCl}(\text{py})_4\}_2(\mu\text{-pz})](\text{PF}_6)_2$  complex (Coe *et al.*, 1993, 1995; Serli *et al.*, 2002). The two *trans*- $[\text{Ru}(\text{py})_4]$  units adopt an eclipsed conformation. The Ru–Br bond distance of 2.5524 (4) Å is significantly longer than that in  $\text{Ru}(\text{TPP})\text{Br}_2$ , 2.425 (2) Å (Ke *et al.*, 1991), owing to the strong  $\sigma$ -donor capacity of the pyridine ligands, although comparable distances have been observed elsewhere (Tomizawa *et al.*, 1994). The average bond angles for pz–Ru–py are 91.57 (10)°, forming a propeller conformation of the four pyridine ligands. The pz–Ru–Br bond is almost linear with an angle of 178.92 (7)°, while py–Ru–py shows a slight tilt with an average angle of 176.14 (10)° [range 174.38 (11)–177.91 (10)°].



**Figure 1**  
View of the cation with atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

## Experimental

[Ru(py)<sub>4</sub>(NO)Br](PF<sub>6</sub>)<sub>2</sub> (300 mg, 0.37 mmol) and NaN<sub>3</sub> (24 mg, 0.37 mmol) were mixed together. Acetone (40 ml) was added and the solution was degassed in the absence of light. After the mixture had been stirred for 1 h, pyrazine (15 mg, 0.18 mmol) was added. This solution was then refluxed for 2.5 h. The solvent was evaporated from the purple solution and the resulting solid was suspended in distilled water and vacuum filtered. The purple product was washed with ether 10 ml and air dried (yield 243 mg). Crystals suitable for X-ray analysis were grown by slow diffusion of ether into a DMF solution of the product.

### Crystal data

[Ru<sub>2</sub>Br<sub>2</sub>(C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>8</sub>](PF<sub>6</sub>)<sub>2</sub> · 2C<sub>3</sub>H<sub>7</sub>NO  
 $M_r = 1510.98$   
 Monoclinic,  $C2/c$   
 $a = 19.0401$  (4) Å  
 $b = 14.6334$  (4) Å  
 $c = 21.2490$  (5) Å  
 $\beta = 90.5609$  (12)°  
 $V = 5920.1$  (2) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.695$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 42564 reflections  
 $\theta = 2.6$ – $27.5^\circ$   
 $\mu = 2.00$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, dark red  
 $0.18 \times 0.10 \times 0.02$  mm

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  scans and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.715$ ,  $T_{\max} = 0.961$   
 21516 measured reflections  
 6741 independent reflections  
 5561 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -24 \rightarrow 24$   
 $k = -18 \rightarrow 18$   
 $l = -27 \rightarrow 27$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.115$   
 $S = 1.07$   
 6741 reflections  
 341 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 4.3116P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.48$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.90$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ru1—Br1	2.5524 (4)	Ru1—N3	2.103 (3)
Ru1—N1	2.095 (3)	Ru1—N4	2.103 (3)
Ru1—N2	2.112 (3)	Ru1—N5	2.079 (3)
N1—Ru1—N2	90.73 (11)	N3—Ru1—N5	93.06 (10)
N1—Ru1—N3	174.38 (11)	N4—Ru1—N5	90.00 (10)
N1—Ru1—N4	91.22 (11)	N1—Ru1—Br1	86.38 (8)
N1—Ru1—N5	92.55 (10)	N2—Ru1—Br1	89.40 (8)
N2—Ru1—N3	89.54 (11)	N3—Ru1—Br1	88.02 (8)
N2—Ru1—N4	177.91 (10)	N4—Ru1—Br1	89.98 (8)
N2—Ru1—N5	90.66 (11)	N5—Ru1—Br1	178.92 (7)
N3—Ru1—N4	88.44 (11)		

During the structure refinement, the atoms of the DMF solvent molecule were observed but could not be modelled satisfactorily. The SQUEEZE routine in PLATON (Spek, 1999) was used to modify the data to account for this, and the solvent was identified as two molecules of DMF per cation. The PF<sub>6</sub><sup>-</sup> anion was disordered over two positions, *A* and *B*, with occupancies of 91 and 9%, respectively. The F atoms of the *B* position were refined isotropically with restrained geometry [P—F bond distances = 1.60 (1) Å]. H atoms were placed in calculated positions and treated as riding atoms (C—H = 0.95 Å), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  (parent C).

Data collection: COLLECT (Nonius, 1997–2001); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 1999); software used to prepare material for publication: SHELXTL.

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## References

- Coe, B. J., Meyer, T. J. & White, P. S. (1993). *Inorg. Chem.* **32**, 4012–4020.  
 Coe, B. J., Meyer, T. J. & White, P. S. (1995). *Inorg. Chem.* **34**, 593–602.  
 Creutz, C. & Taube, H. (1969). *J. Am. Chem. Soc.* **91**, 3988–3989.  
 Fürholz, U., Joss, S., Bürgi, H. B. & Lüdi, A. (1985). *Inorg. Chem.* **24**, 943–948.  
 Ke, M., Sishta, C., James, R. B., Dolphin, D., Sparapan, J. W. & Ibers, J. A. (1991). *Inorg. Chem.* **30**, 4766–4771.  
 Lau, V. C., Berben, L. A. & Long, J. R. (2002). *J. Am. Chem. Soc.* **124**, 9042–9043.  
 Mirza, H. A. & Lever, A. B. P. (2003). In preparation.  
 Nonius (1997–2001). COLLECT. Nonius BV, Delft, The Netherlands.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.  
 Serli, B., Zangrando, E., Ingo, E. & Alessio, E. (2002). *Inorg. Chim. Acta*, **339**, 265–272.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.  
 Sheldrick, G. M. (1999). SHELXTL/PC. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Spek, A. L. (1999). PLATON. Version of October 1999. Utrecht University, The Netherlands.  
 Tomizawa, H., Miki, E., Mizumachi, K. & Ishimori, T. (1994). *Bull. Chem. Soc. Jpn.* **67**, 1816–1824.