Br—Pd—N1^{i}	175.31 (15)	N1—C1—C2	122.4 (6)
N1—Pd—N1^{i}	80.1 (2)	N1—C5—C4	121.6 (6)
Pd—N1—C1	126.5 (5)	N1—C5—C5^{i}	115.2 (5)

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

In order to check the C-centering of the monoclinic lattice, a small sphere of reflections was collected for general reflections *hkl* with $h + k = 2n + 1$. None of those reflections was above the noise level, indicating that the lattice is not monoclinic *P*. H atoms were taken into account at calculated positions riding on their carrier atoms. Final residual features in the difference map are within 0.8 Å of Pd, indicating that the analytical correction for absorption (de Meulenaer & Tompa, 1965) was not completely satisfactory in this case. Test calculations based on additional refinement of an empirical isotropic extinction correction parameter [converging to 0.002 (1)] as implemented in *SHELXL*96 (Sheldrick, 1996) showed marginal improvements [$R(F) = 0.049$, $wR(F^2) = 0.134$ ($\Delta\rho$ range 1.362 to -2.950 e Å^{-3})]. Test calculations based on *DIFABS* as implemented in *PLATON* (Spek, 1990*a*) (correcting for absorption, extinction and other global effects with the same mathematical structure such as overall anisotropic thermal motion) showed that the residual density features near Pd can be largely removed (range $\Delta\rho = 1.04$ to -1.73 e Å^{-3}), resulting in good overall agreement [$R(F) = 0.04$ and $wR(F^2) = 0.107$].

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1990*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*96. Molecular graphics: *PLATON* (Spek, 1990*a*) and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PLATON*.

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References

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Byers, P. K., Canty, A. J., Skelton, B. W. & White, A. H. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1722–1724.
Calvin, G. & Coates, G. E. (1960). *J. Chem. Soc.* pp. 2008–2016.
Canty, A. J., Skelton, B. W., Traill, P. R. & White, A. H. (1992). *Aust. J. Chem.* **45**, 417–422.
Connick, W. B. & Gray, H. B. (1994). *Acta Cryst.* C**50**, 1040–1042.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Hoare, J. L., Hovestad, N., Jastrzebski, J. T. B. H., Canty, A. J., Smeets, W. J. J., Spek, A. L. & van Koten, G. (1997). In preparation.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Livingstone, S. E. (1952). *Proc. R. Soc. NSW*, **86**, 32–37.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Osborn, R. S. & Rogers, D. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1002–1004.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1996). *SHELXL96. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1990*a*). *Acta Cryst.* A**46**, C-34.
Spek, A. L. (1990*b*). *HELENA. Program for Data Reduction.* University of Utrecht, The Netherlands.
Textor, V. M. & Oswald, H. R. (1974). *Z. Anorg. Allg. Chem.* **407**, 244–256.

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trans-Diaquabis(2,2′-bipyridine-*N*,*N*′)-ruthenium(II) Bis(hexafluorophosphate)

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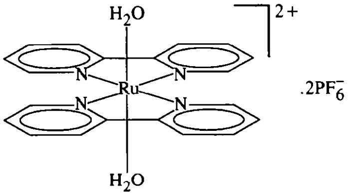
Abstract

The Ru atom of the title complex, $[\mathrm{Ru}(\mathrm{C_{10}H_8N_2})_2(\mathrm{H_2O})_2](\mathrm{PF_6})_2$, is located on a crystallographic inversion center; the bipyridine ligands are bowed [dihedral angle between $\mathrm{C_5N}$ planes is 162.68 (12)°] due to the inter-ligand steric interactions of the *trans* bipyridyl units. The Ru—O distance is 2.116 (2) Å and the mean Ru—N distance is 2.074 (2) Å.

Comment

Octahedral complexes of Ru$^{\rm II}$ and Ru$^{\rm III}$ with *trans* bipyridyl ligands involve non-planar (bowed or twisted) bipyridine units because of inter-ligand steric interactions (Cordes *et al.*, 1982). For the title complex, (I), the pyramidalization angles ($T_{\mathrm{N1C5C6N2}} - T_{\mathrm{C4C5C6N2}} + 180$ and $T_{\mathrm{C4C5C6C7}} - T_{\mathrm{C4C5C6N2}} + 180$) are 7.0 (5) and 5.6 (5)° and the twist angle [$(T_{\mathrm{N1C5C6N2}} + T_{\mathrm{C4C5C6C7}})/2$] is -3.2 (3)°, where T is torsion angle and the calculation is parallel to that used by Dunitz (1979) for analysis of non-planar amide groups. These pyramidalization and twist values are comparable to conformations found for $[\mathrm{Ru(bpy)_2(PPh_3)_2}]^{2+}$ and $[\mathrm{Ru(Me_2bpy)_2py_2}]^{2+}$, where bpy is bipyridine and py is pyridine (Cordes *et al.*, 1982) and indicate that the distortion is primarily a bowing of the bipyridine ligands. The Ru$^{\rm III}$ complex, $[\mathrm{Ru(bpy)_2(H_2O)(OH)}]^{2+}$, which is most comparable to the Ru$^{\rm II}$ title complex, has the twisted conformation (Durham, Wilson, Hodgson & Meyer, 1980). As expected, the Ru$^{\rm III}$ complex has shorter Ru—O distances [2.007 (3) *versus* 2.116 (2) Å]. Consistent with the special affinity and π bonding of Ru^{II} for bipyridyl ligands (Kalyanasundaram, 1992), the Ru—N distances of (I) are shorter than those of the Ru^{III} complex.



(I)

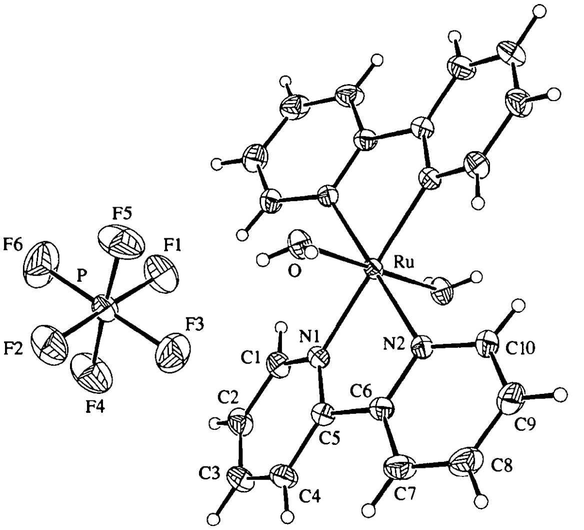


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title complex showing the numbering scheme employed. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

cis-$Ru(bpy)_2Cl_2$ was prepared according to published procedures (Johnson, Sullivan, Salmon, Adeyemi & Meyer, 1978). The title complex was produced as a by-product of the preparation of $[Ru(bpy)_2(qpy)]^{+4}$ (Downard, Honey, Phillips & Steele, 1991) for which $Ru(bpy)_2Cl_2$ and quaterpyridine were heated under reflux in 3:1 ethanol–water for 7 h, followed by addition of NH_4PF_6, which gave a dark brown precipitate. Slow evaporation of the filtrate gave the title complex.

Crystal data

$[Ru(C_{10}H_8N_2)_2(H_2O)_2](PF_6)_2$
$M_r = 739.39$
Triclinic
$P\overline{1}$
$a = 7.5670\,(14)$ Å
$b = 8.7781\,(7)$ Å
$c = 10.2806\,(16)$ Å
$\alpha = 108.941\,(10)°$
$\beta = 94.805\,(14)°$
$\gamma = 98.788\,(11)°$
$V = 631.79\,(16)$ Å^3
$Z = 1$
$D_x = 1.943$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 14–15°$
$\mu = 0.84$ mm^{-1}
$T = 293$ K
Block
0.48 × 0.26 × 0.16 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: analytical
$T_{min} = 0.766$, $T_{max} = 0.891$
2965 measured reflections
2754 independent reflections
2754 reflections with $I_{net} > 0$

$R_{int} = 0.017$
$\theta_{max} = 26.91°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = -13 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 1.2%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.051$
$S = 0.90$
2754 reflections
203 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.0025F^2]$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.080$ e Å^{-3}
$\Delta\rho_{min} = -0.122$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Ru	0	0	0	0.02634 (16)
P	0.04012 (11)	0.61736 (10)	0.30079 (8)	0.0395 (4)
F1	−0.0273 (4)	0.4336 (3)	0.2912 (3)	0.0767 (18)
F2	0.1083 (4)	0.7971 (3)	0.2986 (3)	0.0760 (17)
F3	0.1557 (4)	0.5487 (4)	0.1775 (3)	0.0851 (19)
F4	0.2065 (4)	0.6388 (4)	0.4097 (3)	0.091 (2)
F5	−0.1233 (4)	0.5954 (4)	0.1841 (3)	0.089 (2)
F6	−0.0758 (5)	0.6837 (4)	0.4170 (3)	0.104 (3)
O	−0.0827 (3)	0.2194 (3)	−0.0010 (3)	0.0402 (12)
N1	0.2230 (3)	0.1340 (3)	0.1455 (2)	0.0320 (11)
N2	0.1953 (3)	0.0359 (3)	−0.1228 (2)	0.0323 (11)
C1	0.2480 (4)	0.1564 (4)	0.2825 (3)	0.0402 (16)
C2	0.3937 (5)	0.2617 (4)	0.3725 (3)	0.0469 (17)
C3	0.5228 (5)	0.3492 (5)	0.3235 (4)	0.0515 (18)
C4	0.5030 (4)	0.3224 (4)	0.1820 (4)	0.0467 (17)
C5	0.3547 (4)	0.2141 (3)	0.0963 (3)	0.0340 (13)
C6	0.3362 (4)	0.1604 (3)	−0.0569 (3)	0.0348 (14)
C7	0.4612 (4)	0.2214 (5)	−0.1278 (4)	0.0488 (18)
C8	0.4442 (5)	0.1495 (5)	−0.2702 (4)	0.054 (2)
C9	0.3110 (5)	0.0156 (5)	−0.3356 (3)	0.052 (2)
C10	0.1901 (4)	−0.0390 (4)	−0.2615 (3)	0.0413 (16)

Table 2. *Selected geometric parameters (Å, °)*

Ru—O	2.116 (2)	O—HO2	0.71 (5)
Ru—N1	2.073 (2)	C1—H1	0.99 (4)
Ru—N2	2.075 (2)	C10—H10	0.91 (4)
O—HO1	0.75 (4)		
O—Ru—N1	90.53 (9)	Ru—O—HO1	112 (3)
O—Ru—N2	89.80 (10)	Ru—O—HO2	115 (4)
N1—Ru—N2	77.20 (9)	HO1—O—HO2	111 (5)

The structure was solved using direct methods. H atoms H2–H9 on the bipyridine rings were constrained to idealized (C—H = 0.95 Å) positions and assigned isotropic U values of 0.01 plus the U of the attached C atoms. H1 and H10, the atoms of the inter-ligand contacts responsible for the ligand bowing, were refined isotropically, as were the water H atoms which had been located on difference maps.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1994). Cell refinement: *CAD-4-PC Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX* and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX95*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1040). Services for accessing these data are described at the back of the journal.

References

Cordes, A. W., Durham, B., Swepston, P. N., Pennington, W. T., Condren, S. M., Jensen, R. & Walsh, J. L. (1982). *J. Coord. Chem.* **11**, 251–260.

Downard, A. J., Honey, G. E., Phillips, L. F. & Steele, P. J. (1991). *Inorg. Chem.* **30**, 2259–2260.

Dunitz, J. D. (1979). In *X-ray Analysis and Structure of Organic Molecules*. Ithaca, NY: Cornell University Press.

Durham, B., Wilson, S. R., Hodgson, D. J. & Meyer, T. J. (1980). *J. Am. Chem. Soc.* **102**, 600–606.

Enraf–Nonius (1994). *CAD-4-PC Software*. Version 1.5. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Johnson, E. C., Sullivan, B. P., Salmon, D. J., Adeyemi, S. A. & Meyer, T. J. (1978). *Inorg. Chem.* pp. 2211–2215.

Kalyanasundaram, K. (1992). In *Photochemistry of Polypyridine and Porphyrin Complexes*. San Diego, California: Academic Press.

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trans-Diaquabis(*N*,*N*-diethylnicotinamide-*N*^{1})bis(4-nitrobenzoato-*O*)copper(II)

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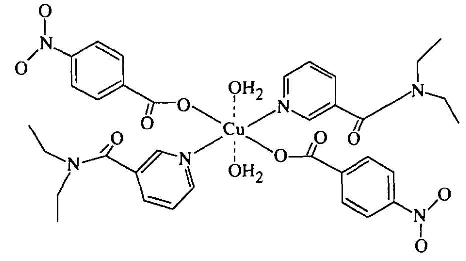
Abstract

The title molecule is a crystallographically centrosymmetric mononuclear complex containing two water molecules, two 4-nitrobenzoato and two diethylnicotinamide ligands, $[Cu(C_7H_4NO_4)_2(C_{10}H_{14}N_2O)_2(H_2O)_2]$, all acting as monodentate ligands. The N and O atoms around the Cu atom form a square-planar arrangement, with the slightly tetragonally distorted octahedral coordination completed by two water O atoms at a distance of 2.485 (2) Å. The water molecules are hydrogen bonded to the carboxyl O atoms [O···O 2.705 (4) Å].

Comment

In the structure analysis of the copper complex of *p*-nitrobenzoic acid (Usubaliev, Amiraslanov, Mamedov & Movsumov, 1980), water molecules were placed in the channels formed by the dimeric $[Cu_2(p\text{-}O_2NC_6H_4COO)_4(H_2O)_2]$ molecules, but two years later, Usubaliev (1982) pointed out that *p*-nitrobenzoic acid molecules were placed in the channels instead of water molecules. The dimeric structure was transformed to a monomeric structure when pyridine was used instead of water as solvent (Usubaliev *et al.*, 1981). Copper(II) benzoate forms both monomeric and dimeric complexes with the pyridine derivative *N*,*N*-diethylnicotinamide, DENA (Hökelek, Gündüz & Necefoğlu, 1996; Hökelek, Necefoğlu & Balcı, 1995).

The structure determination of the title copper complex with two water molecules, two DENA and two 4-nitrobenzoato ligands, (I), was undertaken to understand the effects of the $-NO_2$ and $-C(O)N(C_2H_5)_2$ substituents in the benzoic acid and pyridine molecules. The title monomeric complex, $[Cu(C_6H_4COO.NO_2)_2(DENA)_2.(H_2O)_2]$, has a centre of symmetry and the benzoate ligands are monodentate. The N atoms of the DENA and the O atoms of the benzoate groups form a square-planar coordination around the Cu atom (Table 1). The copper coordination geometry may be considered as slightly tetragonally distorted octahedral since Cu—O6 is 2.485 (2) Å and the angle between Cu—O6 and the normal of the Cu, N1, O1, N1′, O1′ plane is 3.1 (1)° (symmetry operator for primed atoms: $-x$, $-y$, $-z$).



(I)

There are hydrogen bonds between water molecules and the carboxyl O2 atoms [O···O 2.705 (4) Å]. Similar hydrogen bonds are observed in diaquabis[4-hydroxybenzoato)(*N*,*N*-diethylnicotinamide)]cobalt(II) [O···O 2.687 (5) Å; Hökelek & Necefoğlu, 1997], di(*p*-aminobenzoato)tetraaquacobalt(II) [O···O 2.592 (3) Å; Amiraslanov, Mamedov, Movsumov, Musaev & Nadzhafov, 1979] and di(*p*-nitrobenzoato)tetraaquacobalt(II)dihydrate (O···O 2.59 Å; Nadzhafov, Shnulin & Mamedov, 1981). The Cu atom lies 0.740 (2) Å out of the C1, C2, O1, O2 least-squares plane. The Cu—N1 bond length