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trans-Diacetonitrilebis(di-2-pyridyl sulfide-*N*,*N*′)ruthenium(II) bis(tetrafluoroborate) monohydrate

Giuseppe Bruno,* Francesco Nicoló, Giuseppe Tresoldi and Santo Lanza

Dipartimento di Chimica Inorganica Chimica Analitica e Chimica Fisica, Universitá degli Studi di Messina, Via Salita Sperone 31, I-98166 Vill. Sant'Agata, Messina, Italy
Correspondence e-mail: bruno@chem.unime.it

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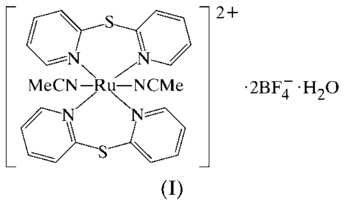
The title complex, $[Ru(C_{10}H_8N_2S)_2(CH_3CN)_2](BF_4)_2\cdot H_2O$, is the product of the solvolysis of $[Ru(dps\text{-}N,N)_2(dps\text{-}N,S)](PF_6)_2$ (dps is di-2-pyridyl sulfide) in the presence of HBF_4 in acetone–acetonitrile at room temperature. There are two independent cations, with the Ru atoms on inversion centres; each Ru atom has an octahedral geometry with the dps molecules behaving as *N*,*N*′-bidentate ligands and assuming a *trans* arrangement.

Comment

Following our interest in the chemistry of the flexible non-planar bipyridine-like ligands (Tresoldi *et al.*, 1991, 1992), we were particularly interested to discover how they would modify the chemical and physical properties of the ruthenium complexes (Bruno *et al.*, 1995; Tresoldi *et al.*, 1996). Recently, taking advantage of the steric hindrance of the *cis*-$Ru(dps\text{-}N,N)_2$ core and steric demands of dps, we were able to introduce into the above centre an *N*,*S*-coordinated dps ligand and provide the possibility for pairs of chemically distinct coordination modes being present in $[Ru(dps\text{-}N,N)_2(dps\text{-}N,S)](PF_6)_2$ (Scopelliti *et al.*, 2001). In this work, the solvolysis of the last complex in the presence of an excess of HBF_4 led to the title complex, (I).



(I)

The title complex is the first example of a ruthenium complex in which two dps ligands adopt a *trans* arrangement.

The IR spectrum contains the characteristic bands of the dps ligand at 1589 (*s*), 1561 (*ms*), 783 (*vs*), 774 (*vs*), 752 (*ms*) and 723 (*s*). The ^1H NMR spectrum in $CD_3(CO)_2$ shows a single *ABMX* system with signals at δ 8.90, assigned to the proton H6 *ortho* with respect to the N atom, δ 7.82, assigned to the proton H5 in the *meta* position, δ 8.34, assigned to the proton H4 in the *para* position and δ 8.00, assigned to the proton H3 *ortho* with respect to the S atom, while the ^{13}C NMR spectrum shows signals at δ 146.87 (C6), 125.13 (C5), 143.18 (C4), 126.82 (C3) and 154.57 (C2). These data are in agreement with the presence of a *trans* isomer which has four equivalent pyridine rings. A *cis* isomer should have only two equivalent pyridyl rings.

Di-2-pyridyl sulfide and its derivatives are flexible ligands that can adopt several possible conformations and dynamic interconvertion depending on their chemical condition (protonated or unprotonated free molecule, chelating or bridging ligand) and on the physical state (Nicoló *et al.*, 1996, and references therein).

The crystal packing of compound (I) shows two complex cations placed on two crystallographic independent inversion centres, in a 1:2 ratio with the tetrafluoroborate anions for charge balance. Both molecules have imposed C_i symmetry and appear equal within experimental error. The dps ligand adopts the twisted *N*,*N*-inside 'butterfly-like' arrangement and the resulting six-membered chelate rings show the usual boat conformation, as evidenced by the puckering analysis (Cremer & Pople, 1975) on the Ru1/N1/C5/S1/C6/N2 [Ru2/N4/C17/S2/C18/N5] ring: $\theta = 88.4\ (2)^\circ$ [88.9 (2)°], $\varphi = 2.4\ (2)^\circ$ [−0.2 (2)°], $Q_T = 0.897\ (2)$ Å [0.898 (2) Å], and $\Delta_S(Ru) = 0.025\ (1)$ [0.001 (1)]. The C and N atoms lie on a plane from which the Ru and S atoms deviate by 0.8148 (1) [0.8055 (1) Å] and 0.743 (1) [0.754 (1) Å] on the same side, respectively. The geometry of the *trans* arrangement of the two chelating dps ligands is very similar to that found in the square-planar palladium cation $[Pd(dps)_2]^{2+}$ (Bruno *et al.*, 1995), showing shorter metal–nitrogen bond lengths, as expected from the different metal atom size. The geometry about the ruthenium(II) ion is distorted octahedral (Fig. 1), with the coordination polyhedron defined by four N atoms of the two opposite chelating dps rings on the equatorial plane and the two acetonitrile N atoms along the axial direction. The Ru–N_{py} bonds are equivalent [average 2.091 (3) Å] but significantly longer than the axial $Ru-N_{ac}$ due to the different electronic and steric properties of the two ligand types and the larger hindrance on the equatorial plane. In fact, the dps chelate bite [average $N_{py}-Ru-N_{py}$ and $N_{py}\cdots N_{py}$ are 88.5 (1)° and 2.918 (5) Å, respectively] is very similar to that in *cis*-$[Ru(dps)_2Cl_2]$ [Bruno *et al.*, 1995; 88.5 (1)° and 2.893 (4) Å] and in one *N*,*N*-chelate ligand in $[Ru(dps)_3]^{2+}$ [Scopelliti *et al.*, 2001; 89.5 (2)° and 2.918 (7) Å]. The main distortion from regular coordination geometry is due to the hindering effect of the S atom on the axial acetonitrile ligand on the same side with respect to the equatorial plane, increasing the $N_{py}-Ru-N_{ac}$ to mean values of 93.5 (1) and 94.5 (1)° in the Ru1 and Ru2 cations, respectively.

In order to understand the structural modifications of the ligand induced by the dps coordination to the metal centre, *ab initio* calculations [HF/6–31+G(d,p) method] were carried out

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on the free ligand using *GAUSSIAN*98 (Frisch *et al.*, 1998). The most important variations concern pyridyl-N atoms; the calculated N—C distances of 1.318 and 1.321 Å in each ring are shorter than the experimental mean value of 1.350 (5) Å, while the computed N···N separation of 3.41 Å is significantly longer, mainly due to the *N,N*-coordination of dps. The calculated C—S bond lengths are slightly longer than the experimental mean value of 1.764 (4) Å], while the C—S—C computed bond angle of 101.5° is very close to the observed average of 102.3 (2)°.

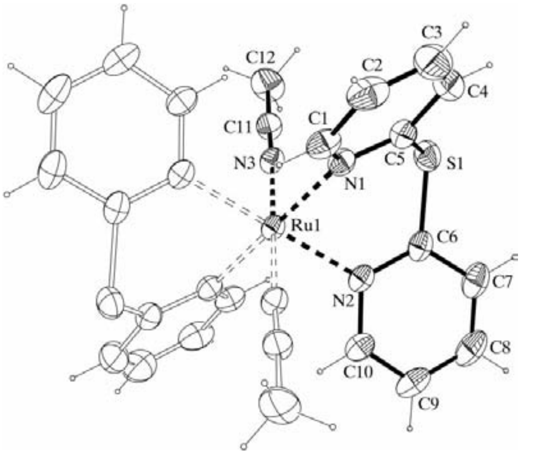

Figure 1
View of one ruthenium complex showing the atomic numbering scheme of the independent fragment. Displacement ellipsoids are drawn at the 30% probability level, while H atoms are of arbitrary size. The unlabelled atoms represent the centrosymmetric (1−*x*, 1−*y*, −*z*) portion of the complex, with the anions and water molecule omitted for clarity.

Experimental

[Ru(dps-*N,N*)$_2$(dps-*N,S*)](PF$_6$)$_2$·H$_2$O was prepared according to the method of Scopelliti *et al.* (2001). All other chemicals were of reagent grade. An acetone–acetonitrile (1:1) solution (5 ml) of [Ru(dps-*N,N*)$_2$(dps-*N,S*)](PF$_6$)$_2$·H$_2$O (48.68 mg, 0.05 mmol) was introduced into a test-tube and 0.1 ml of an aqueous solution of HBF$_4$ (7.65 *M*) added. Diisopropyl ether (8 ml) was layered on top of the reaction mixture and the test-tube was closed with parafilm. After 20 d, colourless crystals were isolated and found to be suitable for X-ray structure investigation. The analysis of $C_{24}H_{24}B_2F_8N_6ORuS_2$ gave C 38.37 *versus* 38.40, H 3.22 *versus* 3.35, N 11.19 *versus* 11.10 and S 8.53 *versus* 8.50% for the calculated and found composition, respectively.

Crystal data

$[Ru(C_2H_3N)_2(C_{10}H_8N_2S)_2](BF_4)_2\cdot H_2O$
$M_r = 751.30$
Triclinic, $P\bar{1}$
$a = 10.0709$ (7) Å
$b = 12.6595$ (8) Å
$c = 13.547$ (1) Å
$\alpha = 77.016$ (7)°
$\beta = 75.004$ (6)°
$\gamma = 68.225$ (6)°
$V = 1533.3$ (2) Å^3
$Z = 2$
$D_x = 1.627$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
$\theta = 8.2$–16.0°
$\mu = 0.73$ mm^{-1}
$T = 298$ (2) K
Prismatic, pale yellow
0.36 × 0.30 × 0.25 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: numerical by seven indexed faces (*XPREPW* in *SHELXTL*; Siemens, 1996)
$T_{min} = 0.689$, $T_{max} = 0.826$
7496 measured reflections
5922 independent reflections
4761 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 26°$
$h = -11 \rightarrow 1$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections every 197 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.085$
$S = 1.06$
5922 reflections
440 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.9658P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.051$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0028 (5)

Table 1
Selected geometric parameters (Å, °).

Ru1—N3	2.022 (2)	Ru2—N6	2.018 (2)
Ru1—N1	2.088 (2)	Ru2—N4	2.091 (2)
Ru1—N2	2.092 (2)	Ru2—N5	2.093 (2)
C5—S1	1.761 (3)	C17—S2	1.768 (3)
S1—C6	1.763 (3)	S2—C18	1.767 (3)
N3—C11	1.127 (4)	N6—C23	1.133 (4)
C11—C12	1.457 (4)	C23—C24	1.458 (4)
N3—Ru1—N1	93.21 (9)	N6—Ru2—N4	94.01 (9)
N3—Ru1—N2	93.75 (9)	N6—Ru2—N5	94.88 (9)
N1—Ru1—N2	88.29 (9)	N4—Ru2—N5	88.61 (9)
N1—C5—S1	120.8 (2)	N4—C17—S2	120.1 (2)
C5—S1—C6	102.3 (1)	C18—S2—C17	102.4 (1)
N2—C6—S1	120.7 (2)	N5—C18—S2	120.7 (2)
C11—N3—Ru1	177.5 (2)	C23—N6—Ru2	171.5 (2)
N3—C11—C12	178.0 (3)	N6—C23—C24	179.9 (4)
N1—C5—S1—C6	49.1 (3)	N4—C17—S2—C18	51.9 (3)
C5—S1—C6—N2	−53.4 (3)	C17—S2—C18—N5	−52.0 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*C*···F4^{i}	0.96	2.38	3.205 (5)	144
O—H0*A*···F2^{ii}	0.87	2.05	2.917 (5)	171
O—H0*B*···F8^{iii}	0.84	2.02	2.83 (1)	162
O—H0*B*···F8*A*^{iii}	0.84	1.96	2.81 (1)	176

Symmetry codes: (i) $1+x, y, z-1$; (ii) $1-x, 1-y, 1-z$; (iii) $1+x, y, z$.

Reflection intensities were evaluated by profile fitting of a '96-steps peak scan among 2θ shells' procedure (Diamond, 1969). H atoms were located in idealized positions and allowed to ride on their parent C atoms with isotropic displacement parameters related to the refined values of their corresponding parent atoms. In the last refinement cycles, the water-H atoms were fixed in idealized positions located by *HYDROGEN* (Nardelli, 1999). Both BF$_4^-$ anions appear to be affected by the usual rotational disorder and one tetrahedral moiety was split over two orientations.

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XPW* in *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *PARST*97, locally modified (Nardelli, 1995) and *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1542). Services for accessing these data are described at the back of the journal.

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