Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

(2,2′-Dipyridyl sulfide-*N*,*N*′)hydroxybis(nitrito-*O*)(nitrogen monoxide-*N*)-ruthenium(III)

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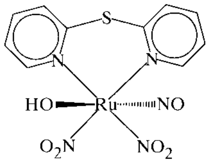
Received 30 July 1999
Accepted 12 November 1999

The title compound, $[Ru(NO_2)_2(OH)(C_{10}H_8N_2S)(NO)]$, is the main product of the reaction between $RuCl_3$ and dps (dps is 2,2′-dipyridyl sulfide, $C_{10}H_8N_2S$) in ethanol–water at room temperature followed by reaction with $NaNO_2$ at a higher temperature. The Ru atom has a distorted octahedral coordination geometry with the dps molecule behaving as an *N*,*N*′-bidentate ligand. The six-membered chelate ring adopts a boat conformation.

Comment

As part of our synthetic work devoted to the incorporation of non-planar bipyridine-like ligands in the coordination sphere of ruthenium with the ultimate aim of modulating the redox properties of Ru centres in binuclear polypyridine complexes (Tresoldi *et al.*, 1996), we recently reported a synthetic method that enabled us to synthesize $[Ru(dps)_2Cl_2]$ (dps is 2,2′-dipyridyl sulfide), and mononuclear and binuclear complexes containing the $Ru(dps)_2$ unit (Bruno *et al.*, 1995). We now report the synthesis and characterization of the title compound, $[Ru(NO_2)_2(OH)(dps)(NO)]$, (I) (Fig. 1), which is the main product of the reaction between $RuCl_3$ and dps in ethanol–water at room temperature for 12 h followed by reaction with $NaNO_2$ at a higher temperature.



(I)

The IR spectrum of (I) contains a broad band at 3529 cm^{-1} and a very strong one at 1867 cm^{-1}, assigned to ν(OH) and ν(NO), respectively. The bands characteristic of the dps ligand are observed at 1591 (*s*), 1556 (*ms*), 778 (*s*), 765 (*s*), 773 (*ms*) and 723 (*s*) cm^{-1}. The ^{1}H and ^{13}C NMR spectra in $(CD_3)_2SO$ show the presence of one *ABMX* system (Tresoldi *et al.*, 1991). The signals of H6, H5, H4 and H3 are observed at δ = 8.73, 8.22, 8.20 and 7.77 p.p.m., respectively, and those of C6, C5, C4 and C3 at δ = 153.6, 141.8, 129.9 and 125.7 p.p.m., respectively. These data are in agreement with the *trans* position of the NO_2 groups with respect the pyridyl rings of dps. In such an arrangement, the two pyridyl rings are equivalent in solution as a result of the rotation of the OH group around the Ru—O bond and of the NO_2 and NO groups around the Ru—N bonds.

As we have already shown (Nicoló *et al.*, 1996, and references therein), 2,2′-dipyridyl sulfide and its derivatives have a flexible skeleton which allows several possible conformations and dynamic interconversions depending on their chemical situation (protonated or unprotonated free molecule, chelating or bridging ligand) and on the state of the material. In the solid state, (I) appears as a 'butterfly'-shaped dps ligand in which the N atom participates in an octahedrally distorted coordination of the Ru atom and the resulting six-membered chelating ring assumes the usual boat conformation. The puckering analysis (Cremer & Pople, 1975) shows the near-perfect boat conformation of the ring [θ = 87.7 (1)°, φ = −1.193 (1)°, Q = 0.983 (1) and $D\sigma$(Ru) = 0.022 (1)]; the C and N atoms lie on a plane from which the Ru and S atoms deviate by 0.909 (1) and 0.802 (1) Å, respectively, on the same side. This is the same situation we have observed already in the analogous Ru^{II}–dichlorobis(2,2′-dipyridyl sulfide) compound (Bruno *et al.*, 1995), where two equivalent dps ligands adopt the usual 'twisted *N*,*N*′-inside' conformation to chelate the metal through the nitrogen lone pairs. Although in (I) the rotation of the pyridine rings shows a slightly smaller dihedral angle [56.8 (1) *versus* 57.5 (1)°] and a correspondingly larger N$\cdots$N bite [2.907 (3) *versus* 2.89 (1) Å], the N_{py}—Ru—N_{py} angle is slightly smaller [86.97 (9) *versus* 88.5 (1)°]. The discrepancy is due to the different *trans* influence of the ligands on the Ru—N_{py} bonds in the two analogous fragments. In $[Ru(dps)_2Cl_2]$, the length of the Ru—N_{py} bonds increases from 2.066 (3) when it is *trans* to the Cl atom to 2.079 (3) Å when it is *trans* to the N_{py} atom, while in (I), it is elongated to 2.112 (2) Å by the opposite NO_2 group (Bruno *et al.*, 1995).

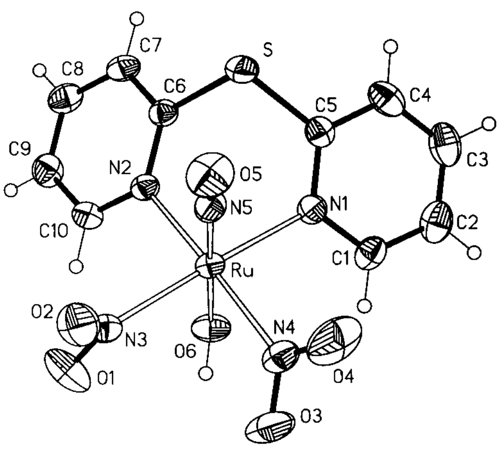


Figure 1
A view of (I) showing the atomic numbering scheme and with displacement ellipsoids at the 50% probability level. H atoms are shown as circles of arbitrary radii.

The dps ligand in (I) has a symmetric butterfly-like arrangement and its pyridine rings form dihedral angles of 42.5 (1) and 43.5 (1)° with the equatorial coordination plane passing through the NO_2 groups. The N3 and N4 nitrites are almost orthogonal to the plane [106.4 (2) and 119.7 (2)°, respectively] to minimize the interference with the adjacent dps rings. The significant difference between the two NO_2 dihedral angles might be related to the presence of an intramolecular hydrogen-bond interaction between the N4 nitrite and the hydroxyl in the axial position: $OH\cdots O3N$ = 2.34 (1) Å. The dps–nitrite interference causes reduction of the $O_2N-Ru-NO_2$ angle and enlargement of the two $O_2N-Ru-N_{py}$ angles [86.4 (1), 92.4 (1) and 94.0 (1)°, respectively] compared with the expected 90°. Therefore, the octahedral geometry of the Ru atom is distorted by the bulky dps ligands as well as by the inequality of the bond lengths to the different coordinated ligands.

Experimental

2,2′-Dipyridyl sulfide was prepared according to the method of Chachaty *et al.* (1976). All other chemicals were reagent grade. Dissolution of bis(2-pyridyl-*N*) sulfide (230 mg, 1.22 mmol) and $RuCl_3\cdot 3H_2O$ (261.5 mg, 1 mmol) in stirred ethanol/water (30 ml; 2:1) yielded a deep-green solution after 12 h at room temperature. The solution was filtered, an aqueous solution (15 ml) of $NaNO_2$ (345 mg, 5 mmol) was added, the temperature was raised to 353 K and the solution was stirred for 30 min. At the end of this period, the solution was allowed to stand at room temperature for 3 h and the yellow solid of $[(Ru(dps)_2(NO_2)_2]$ (Bruno *et al.*, 1995) which formed was filtered off. Yellow crystals of (I) suitable for X-ray analysis were obtained from the filtered solution on standing for *ca* 2 d (yield 50%). Analysis, calculated for $C_{10}H_9N_5O_6RuS$: C 28.04, H 2.12, N 16.35, S 7.48%; found: C 28.10, H 2.14, N 16.30, S 7.55%.

Crystal data

$[Ru(NO_2)_2(OH)(C_{10}H_8N_2S)(NO)]$
M_r = 428.35
Monoclinic, C_2/c
a = 23.802 (4) Å
b = 8.955 (1) Å
c = 13.820 (2) Å
β = 97.55 (1)°
V = 2920.2 (7) Å^3
Z = 8
D_x = 1.949 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
θ = 6.5–15.0°
μ = 1.256 mm^{-1}
T = 298 (2) K
Irregular, yellow
0.26 × 0.24 × 0.12 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968)
T_{min} = 0.785, T_{max} = 0.860
3452 measured reflections
3375 independent reflections
2480 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 27.55°
$h = 0 \rightarrow 30$
$k = 0 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections every 197 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.064
S = 0.879
3375 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.86 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00015 (5)

Table 1
Selected geometric parameters (Å, °).

Ru—N5	1.766 (2)	N1—C5	1.345 (4)
Ru—O6	1.9123 (18)	N1—C1	1.353 (4)
Ru—N3	2.069 (3)	C5—S	1.772 (3)
Ru—N4	2.081 (3)	S—C6	1.770 (3)
Ru—N2	2.110 (2)	C6—N2	1.347 (4)
Ru—N1	2.113 (2)	N5—O5	1.142 (3)
N5—Ru—O6	176.34 (10)	N1—C5—S	119.4 (2)
N3—Ru—N4	86.36 (10)	C6—S—C5	101.32 (14)
N3—Ru—N2	93.96 (10)	N2—C6—S	119.5 (2)
N4—Ru—N1	92.41 (10)	O5—N5—Ru	170.4 (2)
N2—Ru—N1	86.97 (9)		
N1—C5—S—C6	−52.7 (3)	N2—Ru—N3—O2	−109.7 (2)
C5—S—C6—N2	56.7 (3)	N1—Ru—N4—O3	−118.3 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O6-H6A\cdots O3$	0.82	2.34	2.827 (4)	119

Data collection: *P*3/*V* (Siemens, 1989); cell refinement: *P*3/*V*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XPW* (Siemens, 1996); software used to prepare material for publication: locally modified *PARST*97 (Nardelli, 1995) and *SHELXL*97.

We would like to express our gratitude, for support and aid, to the Italian MURST and CNR and to the Centro Interdipartimentale di Servizi per la Diffrattometria a Raggi X of the University of Messina.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1084). Services for accessing these data are described at the back of the journal.

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