

A complex containing three different kinds of Ru—N bonds: ethoxydinitro-nitrosyl(*N,N,N',N'*-tetramethylethylenediamine- κ^2N,N')ruthenium(II)

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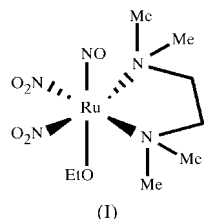
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The octahedral title compound, [Ru(C₂H₅O)(NO)(NO₂)₂·(C₆H₁₆N₂)], crystallizes in the rhombohedral space group *P*3₁ with an ethoxy ligand axially coordinated *trans* to the nitrosyl ligand. The Ru^{II} ion is equatorially coordinated by a tetramethylethylenediamine group acting as a bidentate ligand, and to two nitro moieties whose planes are tilted with respect to the mean equatorial plane. Each nitrogen ligand bonded to the metallic centre has a different hybridization state.

Comment

We are interested in the chemistry of Ru–nitrosyl complexes bearing electron-donor ligands. The chemistry of metallo-nitrosyl complexes and redox-related NO complexes is relevant to the understanding of the rich biochemistry of nitric oxide. These complexes are also useful synthetic precursors, as the reactivity of the NO⁺ group frequently allows its substitution by a variety of ligands, enhancing the potential of such compounds as building blocks for more complex structures.

The title compound, (I), was obtained by reaction of the electron-rich TMED ligand (TMED is tetramethylethylenediamine) and Ru^{II}(dmsO)₄Cl₂ (dmsO is dimethylsulfoxide) in a reductive environment, followed by addition of NaNO₂.



Complex (I) is a rare case in which three kinds of Ru–N bonds, each corresponding to different types of hybridization

of the N atom, are present in the same molecule (Fig. 1). Ru–ligand bond distances vary from 1.754 (9) to 2.205 (9) Å (Table 1). The Ru^{II} ion is in an octahedral environment, mainly distorted by the limited N–Ru–N bite angle [82.4 (3)°] of the bidentate TMED group.

The TMED ligand is bonded to the Ru^{II} atom with the longest Ru–N distance in the molecule [mean 2.20 (2) Å]. This distance is slightly longer than those found in Ru–ethylenediamine complexes due to the electronic influence of the methyl moieties [see, for example, Ru(ethylenediamine)₃²⁺; Smolenaers *et al.*, 1981]. The TMED N atoms adopt an *sp*³ conformation, as evidenced by the observed bond angles. All the methyl groups in the TMED ligand adopt a staggered conformation with respect to the H atoms of the neighbouring methylene.

The average Ru–NO₂ bond distance in (I) is 2.11 (2) Å. The N atoms belonging to the nitro ligands can be regarded as approximately *sp*²-hybridized. The mean Ru–N bond distance in Ru(py)₆²⁺ (py is pyridine; Templeton, 1979) is 2.12 Å, similar to the mean Ru–NO₂ bond distance observed in (I). The shorter Ru–N distances reflect the π back-bonding between the metal and the ligand. The Ru atom is essentially in the plane of each NO₂ group. Due to steric hindrance, the planes of the nitro ligands (Ru/N4/O3/O4 and Ru/N5/O5/O6; Fig. 1) are rotated with respect to the equatorial plane (Ru/N2/N3/N4/N5) by 51.2 (4) and 45.0 (5)°, respectively.

The Ru–N1–O1 angle is essentially linear [171 (1)°], indicating that the complex can be described as an [Ru^{II}–NO⁺] moiety. The Ru–NO bond length is 1.754 (9) Å; this is the shortest Ru–ligand distance in the complex, as expected from the effect of strong π back-bonding. These geometric parameters indicate an *sp*-hybridization for the nitrosyl N atom. The N–O bond distance in the nitrosyl is rather large [1.16 (1) Å] compared with other Ru–nitrosyl complexes (see, for example, Wescott & Enemark, 1999). This is probably related to the presence of the ethoxy group *trans* to the nitrosyl, as has been shown previously by Hagihara *et al.* (2000). This interaction is also responsible for the short Ru–O2 bond distance observed for the ethoxy group [1.898 (7) Å], which is in good agreement with what has been observed for

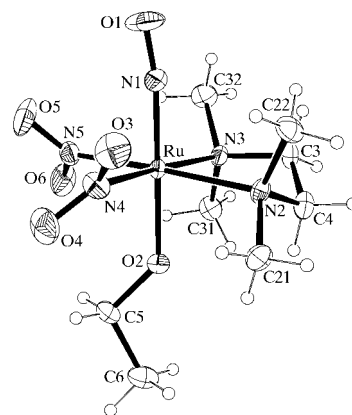


Figure 1

A view of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

other Ru–nitrosyl complexes with a *trans* hydroxy ligand (Wong *et al.*, 1992; Bruno *et al.*, 2000).

In summary, compound (I) is the first example of an Ru complex in which the metal is bonded to N atoms in three different hybridization states. The remarkable differences in the bond distances give an excellent illustration of the different kinds of interaction between the metal and each ligand.

Experimental

The precursor compound, *trans*-RuCl₂(dmsO)₄, was synthesized as described by Evans *et al.* (1973). Tetramethylethylenediamine (TMED) was distilled from metallic sodium under an inert atmosphere before use. The other reagents were used as provided. TMED (1.10 g, 10 mmol) was added to a solution of *trans*-RuCl₂(dmsO)₄ (102 mg, 0.21 mmol) in ethanol (30 ml). The solution was refluxed for 90 min; the colour of the solution changed from yellow to pale orange. The solvent was then removed under vacuum and the solid product washed with diethyl ether. This product was dissolved in degassed ethanol under an argon atmosphere, and Zn/Hg was added. After stirring for 30 min, the solution was filtered using Schlenk techniques. NaNO₂ (0.35 g, 5 mmol) was added to the filtrate and the suspension was refluxed for 40 min under argon. After removing the excess NaNO₂ by filtration, the solvent was removed under vacuum. The orange product obtained was washed several times with distilled water and dried over silica under vacuum. The crude product was dissolved in CH₂Cl₂ and loaded onto a silica column with 1:1 CH₂Cl₂/MeOH elution of the desired product. The selected fraction was dried, yielding 10 mg of an orange solid (yield 13%). Single crystals of (I) were grown at 254 K by slow diffusion of diethyl ether into an acetonitrile solution of the orange product.

Crystal data

[Ru(C ₂ H ₅ O)(NO)(NO ₂) ₂ (C ₆ H ₁₆ N ₂)]	Cu K α radiation
$M_r = 384.37$	Cell parameters from 25 reflections
Trigonal, $P3_1$	$\theta = 10.1\text{--}21.6^\circ$
$a = 7.930$ (2) Å	$\mu = 8.97$ mm ⁻¹
$c = 20.210$ (9) Å	$T = 293$ (2) K
$V = 1100.6$ (6) Å ³	Prism, dark orange
$Z = 3$	$0.08 \times 0.06 \times 0.06$ mm
$D_x = 1.740$ Mg m ⁻³	

Data collection

Enraf–Nonius CAD-4 diffractometer	1431 reflections with $I > 2\sigma(I)$
Non-profiled $\omega/2\theta$ scans	$R_{\text{int}} = 0.045$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 69.8^\circ$
$T_{\text{min}} = 0.439$, $T_{\text{max}} = 0.566$	$h = 0 \rightarrow 9$
1593 measured reflections	$k = -9 \rightarrow 0$
1398 independent reflections (plus 41 Friedel-related reflections)	$l = 0 \rightarrow 24$
	1 standard reflection
	frequency: 30 min
	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 4.2825P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.094$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.15$	$\Delta\rho_{\text{max}} = 0.87$ e Å ⁻³
1439 reflections	$\Delta\rho_{\text{min}} = -1.72$ e Å ⁻³
207 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.04 (2)

During the refinement process, about two-thirds of the H atoms in the molecule were found among the first 25 peaks of the difference

Table 1

Selected geometric parameters (Å, °).

Ru–N1	1.754 (9)	Ru–N3	2.185 (9)
Ru–O2	1.898 (7)	Ru–N2	2.205 (9)
Ru–N5	2.10 (1)	N1–O1	1.16 (1)
Ru–N4	2.11 (1)		
N1–Ru–O2	176.8 (4)	N5–Ru–N2	174.0 (4)
N1–Ru–N5	87.9 (4)	N4–Ru–N2	94.3 (4)
O2–Ru–N5	93.3 (4)	N3–Ru–N2	82.4 (3)
N1–Ru–N4	86.3 (4)	O1–N1–Ru	171 (1)
O2–Ru–N4	90.7 (4)	C4–N2–Ru	105.0 (6)
N5–Ru–N4	90.6 (4)	C3–N3–Ru	105.7 (6)
N1–Ru–N3	94.7 (4)	O4–N4–Ru	120.8 (8)
O2–Ru–N3	88.2 (3)	O3–N4–Ru	117.7 (8)
N5–Ru–N3	92.7 (3)	O6–N5–Ru	122.0 (8)
N4–Ru–N3	176.6 (4)	O5–N5–Ru	117.7 (9)
N1–Ru–N2	95.8 (4)	C5–O2–Ru	134.7 (7)
O2–Ru–N2	83.3 (3)		

Fourier map. However, all H atoms were positioned stereochemically and refined with a riding model (C–H = 0.96 or 0.97 Å). The methyl groups were treated in the refinement as rigid bodies and allowed to rotate around the corresponding C–C bond.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1216). Services for accessing these data are described at the back of the journal.

References

- Bruno, G., Nicolo, F. & Tresoldi, G. (2000). *Acta Cryst.* **C56**, 282–283.
- Enraf–Nonius (1994). CAD-4 EXPRESS. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
- Evans, I. P., Spencer, A. & Wilkinson, G. (1973). *J. Chem. Soc. Dalton Trans.* pp. 204–209.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hagihara, T., Ikezawa, H., Tomizawa, H. & Miki, E. (2000). *Inorg. Chim. Acta*, **299**, 80–90.
- Harms, K. (1995). XCAD4. University of Marburg, Germany.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Smolenaers, P. J., Beattie, J. K. & Hutchinson, N. D. (1981). *Inorg. Chem.* **20**, 2202–2206.
- Templeton, J. L. (1979). *J. Am. Chem. Soc.* **101**, 4906–4917.
- Wescott, B. L. & Enemark, J. H. (1999). *Inorganic Electronic Structure and Spectroscopy*, Vol. II, edited by E. I. Solomon & A. B. P. Lever, pp. 403–450. New York: John Wiley and Sons.
- Wong, K.-Y., Che, C.-M., Yip, W.-H., Wang, R.-J. & Mak, T. C. W. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1417–1421.