Preparation and Characterization of Nitrosylruthenium(III) Complexes Containing Diethylenetriamine

Risa ASANUMA, Hiroshi TOMIZAWA,* Akio URUSHIYAMA, Eiichi MIKI,*
Kunihiko MIZUMACHI, and Tatsujiro ISHIMORI
Department of Chemistry, College of Science, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171
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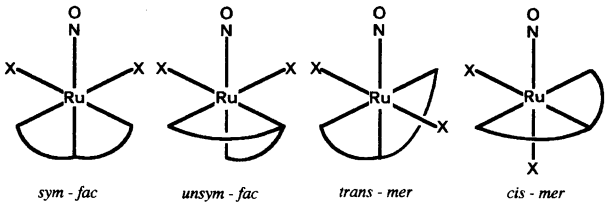
Some kinds of $\{Ru^{II}\text{-}NO^{+}\}$-type complexes containing a diethylenetriamine ligand were prepared from hydrous $RuX_3 \cdot NO$ (X=Cl or Br) and diethylenetriamine. Among them, the crystal and molecular structures for *trans-mer*-$[RuCl_2(dien)NO]PF_6$ (**1**) and *mer*-$[RuBr_3(Hdien)NO]Br \cdot H_2O$ (**2**) (dien=diethylenetriamine) were determined by X-ray diffraction. The crystal of **1** was monoclinic, space group $P2_1/a$ with a=21.296(4), b=6.602 (2), c=10.079(2) Å, β=97.12(2)°, Z=4, and final R=0.0307, and the crystal of **2** was orthorhombic, space group $P2_12_12_1$ with a=11.988(4), b=17.234(9), c=7.141(2) Å, Z=4, and final R=0.0825. In **1**, the two chloro ligands were in the *trans* arrangement and the dien was in the *meridional* arrangement as a tridentate ligand. In **2**, the three bromo ligands were in the *meridional* arrangement with the Hdien coordinated to the ruthenium through one terminal and central nitrogen atoms as a bidentate ligand, and the remaining uncoordinated terminal moiety was $-NH_3^+$. The *trans*-strengthening effect that is expected to be caused by the NO was not observed for the Ru–N(dien) bond. The synthesized complexes were also characterized by IR and NMR spectra.

Nitrosylruthenium(III) complex with a linear Ru–N–O bond has been extensively studied from the viewpoint of the *trans*-strengthening effect caused by the nitrosyl group, and the effect has been explained from the inherent property of the NO, a strong π-acceptor and a weak σ-donor.[1] For *cis*-$[RuCl(qn)_2NO]$ (Hqn=8-quinolinol[2] or 2-methyl-8-quinolinol[3]) containing the bidentate ligand (qn), which shows both π- and σ-donor abilities on coordination, the *trans*-strengthening effect was observed on the bond between the ruthenium and the ligating oxygen atom of the qn; the Ru–O(1) bond where the O(1) is *trans* to the NO is shorter than the Ru–O(2) bond where the O(2) is *cis* to the NO. However, for the nitrosylruthenium(III) complexes containing the ligands that show only σ-donor ability on coordination, contribution of the σ-donor ability to the *trans*-strengthening effect has not been investigated except for the ammine complexes. We have reported structures of *mer*-$[RuX_3(en)NO]$ (X=Cl, Br, and I) containing an ethylenediamine ligand that shows only σ-donor ability on coordination. The *trans*-strengthening effect was not observed on the Ru–N(en) bond.[4]

Diethylenetriamine (dien) also shows σ-donor ability only on coordination. The possible structures of the nitrosylruthenium(III) complexes containing a dien as a tridentate ligand are shown in Scheme 1. Among these geometrical isomers, Kushi et al. have already prepared *sym-fac*- and *unsym-fac*-$[RuCl_2(dien)NO]I$ by the reaction of *fac*-$[RuCl_3(dien)]$ with $NaNO_2$ in an acidic medium, and studied them by X-ray diffraction and NMR measurements.[5] The X-ray diffraction study showed that the *trans*-strengthening effect that is expected to be caused by the NO is not observed for the Ru–N(dien) bond.

In this study, we have attempted to prepare the remaining geometrical isomers, *trans-mer*- and *cis-mer*-$[RuCl_2(dien)NO]^+$, by the reaction of hydrous $RuCl_3 \cdot NO$ with dien, and prepared *trans-mer*-$[RuCl_2(dien)NO]Y$ (Y = I or PF_6) and *mer*-$[RuBr_3(Hdien)NO]Br \cdot H_2O$, in the latter of which the Hdien coordinates as a cationic bidentate ligand. The structures have been determined by X-ray diffraction and studied using NMR and IR spectra. However, the *cis-mer* isomer could not be prepared.



Scheme 1.

Experimental

Measurements. The UV-vis spectra of the complexes in H_2O were measured with a Hitachi U-3410 spectrometer. The infrared spectra were measured by a Nujol mull method with JASCO A-202 (4000—400 cm^{-1}) and JASCO IR-F (700—200 cm^{-1}) spectrometers. The ^1H, ^{13}C, COSY (correlation spectroscopy), and C–H COSY NMR spectra were recorded on a JEOL GSX-400 spectrometer by using DMSO-d_6 as a solvent and TMS as an internal standard.

Preparation of Compounds. *trans-mer*-$[RuCl_2(dien)NO]Y$ (Y=I or PF_6(1)): Hydrous $RuCl_3 \cdot NO$ (1 mmol) was dissolved in hot 0.1 mol dm^{-3} HCl (20 cm^3). The solution was adjusted to pH 6.5 with 0.1 mol dm^{-3} NaOH and was refluxed for 1 h. An agueous solution of dien (1 mmol in 15 cm^3) partially neutralized with HCl (pH about 4) was added to the refluxed solution and then 0.1 mol dm^{-3} NaOH was added to pH 6.5. This solution was refluxed again for 3 h and was evaporated on a rotary evaporator. The crude product was dissolved in 100 cm^3 of water and put on a cation-exchange column (ϕ 2×14 cm) of SP-Sephadex C-25 (H^+ form). The adsorbed complexes were eluted with 0.2 mol dm^{-3} HCl. The orange

eluate obtained as the major first band was evaporated on a rotary evaporator. The orange solid was triturated with ethanol, filtered, washed with ethanol, and air dried. The compound was dissolved in a minimum of water, and then an excess of NaI was added to the cold solution to give yellowish-brown crystals, which were collected by filtration and washed with a saturated aqueous solution of sodium iodide, cold water, and ethanol successively, and air dried; yield 22%. For preparation of the single crystals and for the measurement of the UV-vis spectrum, the hexafluorophosphate salt (**1**) was used. Found (iodide): C, 11.3; H, 2.6; N, 12.7; Cl, 16.2; I, 29.3%. Calcd for $C_4H_{13}N_4OCl_2IRu$: C, 11.1; H, 3.0; N, 13.0; Cl, 16.4; I, 29.4%. Found (hexafluorophosphate): C, 12.9; H, 3.4; N, 18.5; Cl, 19.8%. Calcd for $C_4H_{13}N_4OCl_2PF_6Ru$: C, 13.1; H, 3.5; N, 19.1; Cl, 19.4%. IR ν(NO) at 1873 and ν(RuCl) at 347 cm^{-1} for the iodide; ν(NO) at 1892 cm^{-1} and ν(RuCl) at 344 cm^{-1} for the hexafluorophosphate. UV 20000 (ε/mol^{-1} dm^3 cm^{-1} 15, sh), 24000 (ε 49, sh), 28000 (ε 87), and 33300 cm^{-1} (ε 141).

***mer*-[RuBr$_3$(Hdien)NO]Br·H$_2$O(2):** An aqueous solution of dien (3 mmol in 10 cm^3) partially neutralized with HBr (pH about 4) was added to an 0.1 mol dm^{-3} HBr solution of hydrous $RuBr_3$·NO (2 mmol in 20 cm^3). The solution was adjusted to pH 4 with dilute HBr, was refluxed for 2 h, and then the resultant solution was evaporated on a rotary evaporator. The same column chromatography as used for the chloro complex was applied using 0.2 mol dm^{-3} HBr as an eluent. The brown eluate collected as the major band was evaporated on a rotary evaporator. For further purification, the same column chromatography was used. The reddish-brown eluate obtained as the major second band was concentrated on a rotary evaporator to about 10 cm^3, whereupon dark-purple crystals were deposited. The crystals were collected by filtration, washed with cold water and ethanol, and air dried; yield 30%. Found: C, 8.4; H, 2.5; N, 9.8; Br, 56.9%. Calcd for $C_4H_{16}N_4O_2Br_4Ru$: C, 8.4; H, 2.8; N, 9.8; Br, 55.9%. IR ν(NO) at 1870 ν(RuBr) at 270 cm^{-1}. UV 18800 (ε/mol^{-1} dm^3 cm^{-1} 49, sh) and 20700 cm^{-1} (ε 66).

X-Ray Crystal Analysis. To obtain crystals suitable for the structural analysis, 30 mg of **1** or 50 mg of **2** was dissolved in 5 cm^3 of water or 10 cm^3 of aqueous HBr (pH 4). The solution was allowed to evaporate at room temperature. Several days after, dark orange columnar (**1**) or dark purple plate (**2**) crystals were obtained.

For crystals of **1** and **2**, a similar method of reflection data collection was used. Crystal data and experimental conditions for intensity collection are shown in Table 1. Preliminary Weissenberg photographs taken with Cu $K\alpha$ radiation (λ=1.54184 Å) showed that **1** was monoclinic and **2** was orthorhombic. The crystals were transferred to Rigaku AFC-5 automated four-circle diffractometer and intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at room temperature. The lattice parameters were obtained by the least-squares refinement using 20 reflections ($20°\leq 2\theta \leq 25°$ for **1** and $20°\leq 2\theta \leq 21°$ for **2**). For weak reflections, measurements were repeated up to four times. Crystal stability was monitored by recording three standard reflections after every 100 reflections, and no significant variations were observed. For the structure determination and refinement, intensity data of unique reflections with $|F| \geq 3\sigma(|F|)$ from collected reflections were used. Intensities were corrected for Lorentz and polarization effects. The absorption correction was applied by the published method of North et al.[6] All calculations were made on a HITAC 680H computer by using the UNICS III Program System[7] at the Computer Center of the University of Tokyo. The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. For **1**, all of hydrogen atoms were observed in difference Fourier syntheses and were included in the refinement. The final R value was 0.0307 with anisotropic temperature factors for all atoms except hydrogen atoms and with isotropic factors for hydrogen atoms. For **2**, several electron density peaks that could be assigned to hydrogen atoms were observed indifference Fourier syntheses but these were not included in the refinement, and the final R value was 0.0825 with anisotropic temperature factors. The atomic scattering factors were taken from the standard sources[8] for non-hydrogen atoms and from the published data of Stewart et al.[9] for hydrogen atoms. The positional and thermal parameters are given in Table 2.

Tables of anisotropic thermal parameters, coordinates of hydrogen atoms and the complete $F_o - F_c$ data are deposited as Document No. 67023 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Crystal and Molecular Structures. ORTEP drawings of the complex cations of **1** and **2** are shown in Figs. 1 and 2, respectively. The selected intramolecular bond lengths and angles in the complex cations are shown in Table 3. In both **1** and **2**, the NO is essentially colinear with the ruthenium atom and the Ru–NO and the N–O bond lengths are similar to the typical values in other linear nitrosylruthenium(III) complexes,[2—4,10—15] indicating that the NO coordinates to the ruthenium(II) formally as NO^+. The Ru–X (X=Cl or Br) bond lengths are also typical of those observed in other ruthenium(II) complexes containing halogeno ligands.[2,3,10—16]

Structure of 1: The two chlorine atoms are in the

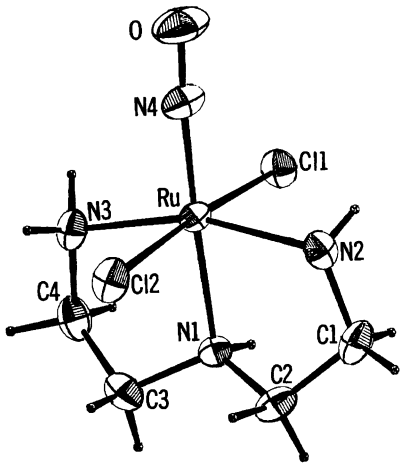


Fig. 1. ORTEP drawing and atomic numbering scheme of *trans-mer*-$[RuCl_2(dien)NO]^+$ cation in *trans-mer*-$[RuCl_2(dien)NO]PF_6$ (**1**).

Table 1. Crystal Data and Experimental Conditions for Intensity Collection

Parameter	*trans-mer*-[$RuCl_2$(dien)NO]PF_6 (**1**)	*mer*-[$RuBr_3$(Hdien)] (**2**)
Formura	$RuCl_2PF_6ON_4C_4H_{13}$	$RuBr_4O_2N_4C_4H_{16}$
NW	450.15	572.20
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/a$	$P2_12_12_1$
a/Å	21.296(4)	11.988(4)
b/Å	6.602(2)	17.234(9)
c/Å	10.079(2)	7.141(2)
β/°	97.12(2)	
V/Å^3	1399.6(5)	1475.4(10)
Z	4	4
D_m/g cm^3	2.12	2.54
D_c/g cm^3	2.14	2.58
Crystal size/mm	0.1×0.3×0.3	0.1×0.2×0.2
μ(Mo $K\alpha$/cm^{-1})	16.61	117.69
F(000)	880	1072
Scan mode	ω–2θ	ω–2θ
Scan width	1.10+0.45 tan θ	1.10+0.42 tan θ
No. of reflections collected	3701	1985
No. of reflections with $\|F\| \geqq 3\sigma$ ($\|F\|$)	2308	1791
R[a)]	0.0307	0.0825
R_w[b)]	0.0410	0.0986

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $R_w=(\sum w(||F_o|-|F_c||)^2/\sum w|F_o|^2)^{1/2}$ ($w=1$).

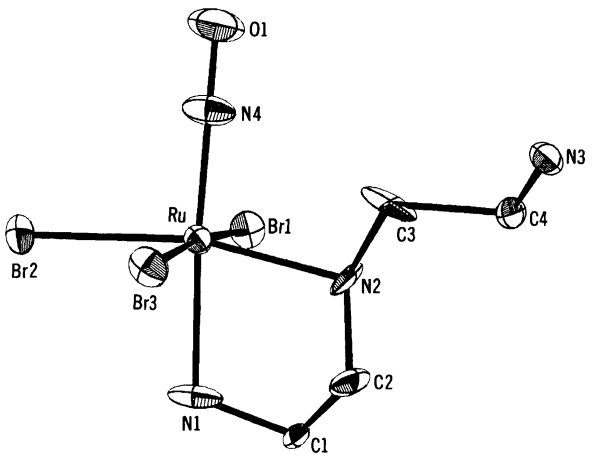


Fig. 2. ORTEP drawing and atomic numbering scheme of *mer*-[$RuBr_3$(Hdien)NO]$^+$ cation in *mer*-[$RuBr_3$(Hdien)NO]Br·H_2O (**2**).

trans arrangement and in a position *cis* to the NO. The three nitrogen atoms of the dien ligand are in the *meridional* arrangement and the central nitrogen atom (N1) is in a position *trans* to the NO.[17] The two chelate rings formed by the diethylenetriamine have a gauche conformation and show no significant distortion. The Ru atom is displaced by 0.138(1) Å toward the NO group out of the best plane consisting of the two chlorine and the two nitrogen (N2 and N3) atoms.[18] The same distortion has been found in *mer*-[RuX_3(en)NO] (X=Cl, Br, or I), which is attributed to the bulky Ru–NO bond orbital.[4] The bond of the Ru–N1 is shorter than those of the Ru–N2 and the Ru–N3 as observed for the *sym-fac* and *unsym-fac* isomers.[5]

Structure of 2: The three bromine atoms are in the *meridional* arrangement and in a position *cis* to the NO. The central nitrogen atom (N2) coordinates to the ruthenium in a position *cis* to the NO, one of the terminal nitrogen atoms (N1) is in a position *trans* to the NO, and the other nitrogen atom (N3) does not coordinate. Thus, the complex cation has only one chelate ring. Figure 3 shows a view of the packing around the uncoordinated terminal nitrogen atom (N3). The terminal nitrogen atom (N3) is tetrahedrally surrounded by

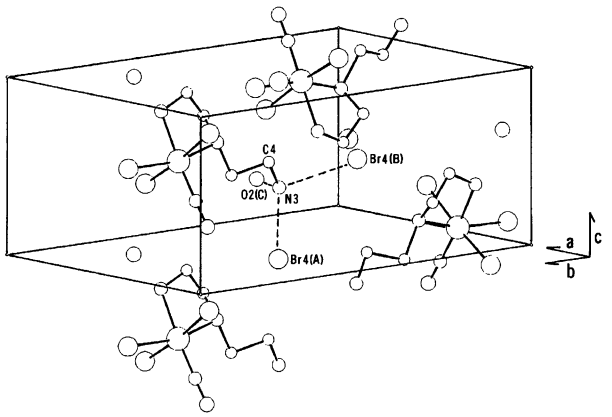


Fig. 3. View of packing around N3 in *mer*-[$RuBr_3$(Hdien)NO]Br·H_2O (**2**). Key to symmetry operation: A: $x,y,z-1$; B: $-x+1/2$, $-y+1$, $z+1/2-1$; C: $-x,y+1/2$, $-z+1/2$.

Table 2. Positional and Thermal Parameters with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}[a)]/Å^2
	trans-mer-[$RuCl_2$(dien)NO]PF_6 (**1**)			
Ru	0.15292(2)	0.44850(5)	0.17074(3)	2.5
Cl1	0.20881(6)	0.1824(2)	0.2891(1)	3.7
Cl2	0.08922(7)	0.7115(2)	0.0667(1)	4.1
P	0.10867(7)	0.1645(3)	−0.3063(1)	4.1
F1	0.0594(2)	0.1736(9)	−0.2035(4)	9.4
F2	0.0922(3)	−0.0587(9)	−0.3254(6)	12.5
F3	0.0570(2)	0.232(1)	−0.4167(5)	13.4
F4	0.1620(2)	0.118(1)	−0.1899(5)	11.0
F5	0.1482(2)	0.156(1)	−0.4059(5)	12.4
F6	0.1249(3)	0.3880(8)	−0.2830(8)	14.3
O	0.2410(2)	0.4333(9)	−0.0251(5)	7.0
N1	0.0953(2)	0.4429(6)	0.3240(4)	3.0
N2	0.2005(2)	0.6678(6)	0.2978(4)	3.5
N3	0.0838(2)	0.2406(6)	0.0871(4)	3.5
N4	0.2044(2)	0.4429(7)	0.0489(4)	4.0
C1	0.1717(3)	0.6790(9)	0.4255(5)	4.4
C2	0.1025(3)	0.6355(8)	0.3994(5)	4.1
C3	0.0312(2)	0.3707(9)	0.2715(6)	4.2
C4	0.0398(2)	0.1903(8)	0.1866(6)	4.2
	mer-[$RuBr_3$(Hdien)NO]Br·H_2O (**2**)			
Ru	0.1102(2)	0.1585(1)	0.1186(4)	2.2
Br1	0.2826(3)	0.1523(2)	0.3153(5)	3.0
Br2	0.0991(3)	0.0131(2)	0.1137(6)	3.7
Br3	−0.0735(3)	0.1652(2)	−0.0504(5)	3.7
Br4	0.2471(3)	0.3823(2)	0.5362(5)	3.0
O1	0.245(3)	0.169(2)	−0.223(4)	6.9
O2	0.119(3)	0.024(2)	0.632(5)	6.8
N1	0.022(2)	0.157(2)	0.381(4)	4.0
N2	0.107(3)	0.278(1)	0.192(4)	4.0
N3	0.112(2)	0.463(1)	−0.114(5)	3.6
N4	0.189(2)	0.165(2)	−0.089(4)	4.2
C1	0.022(3)	0.236(2)	0.464(4)	2.4
C2	0.014(3)	0.291(2)	0.317(5)	3.5
C3	0.094(3)	0.329(3)	−0.011(4)	5.0
C4	0.132(3)	0.420(2)	0.046(5)	3.0

a) $B_{eq}=4/3\sum_i\sum_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

the carbon atom (C4), the two bromide ions, and the oxygen atom of the crystal water. These interatomic bond lengths and angles are also shown in Table 3. These data and the NMR study mentioned later show that the three hydrogen atoms are between the N3 and the bromide ions and between the N3 and the oxygen of the crystal water, so that the uncoordinated terminal moiety is $-NH_3^+$.[19] The bond lengths and angles in the chelate ring are comparable to those in **1** or in the analogous dien complexes.[5] However, the bond lengths and angles around the uncoordinated moiety seem to be unusual; a large anisotropy of the temperature factor was found for the N1, N2, and C3. Thus, reexamination of the atomic positions on the Fourier map or the difference Fourier map was attempted but a more suitable atomic position or disorder could not be found. The Ru atom was displaced by 0.121(4) Å toward the NO group out of the best plane consisting of the three bromine and the nitrogen (N2) atoms,[20] as found in **1**. The Ru–N2 bond was found to be shorter than the Ru–N1 bond, though the difference was not apparent considering the standard deviations.

It is well-known that the NO group causes a *trans*-strengthening effect in the {Ru^{II}–NO^+}-type complex, and the effect has been explained from the nature of the NO as a strong π-acceptor and a weak σ-donor.[1] The study of X-ray crystal analysis of $A_2[RuCl_5NO]$ (A=NH_4 or K) shows that the Ru–Cl (*trans* to the NO) bond is shorter than the Ru–Cl (*cis* to the NO) bond because the σ-bonding ability of Cl^- is stronger than that of NO^+.[13,14] On the other hand, the LCAO MO calculation on RuX_5NO-type complexes (X=H_2O, NH_3, Cl^-, or CN^-) shows that the *trans*-strengthening effect is attributable to both the σ-bonding and π-bonding effects, though the σ-effect is the most important.[21,22] Thus, the *trans*-strengthening effect was expected for the bonds between the Ru and dien, which behaves as a σ-donor on coordination. In **1**, the Ru–N1 bond in a

Table 3. Selected Bond Lengths (Å) and Angles (°) with Their Estimated Standard Deviations in Parentheses

		trans−*mer*−[$RuCl_2$(dien)NO]PF_6 (**1**)			
Ru–Cl1	2.359(1)	Ru–N4	1.745(4)	C3–C4	1.500(8)
Ru–Cl2	2.364(1)	N2–C1	1.493(8)	C4–N3	1.487(7)
Ru–N1	2.084(4)	C1–C2	1.486(8)	N4–O	1.140(7)
Ru–N2	2.104(4)	C2–N1	1.480(7)		
Ru–N3	2.108(4)	N1–C3	1.475(7)		
Cl1–Ru–Cl2	174.33(5)	Cl2–Ru–N4	94.4(2)	N2–C1–C2	109.7(4)
Cl1–Ru–N1	85.2(1)	N1–Ru–N2	80.9(2)	C2–N1–C3	119.6(4)
Cl1–Ru–N2	91.8(1)	N1–Ru–N3	80.9(2)	C2–N1–Ru	109.5(3)
Cl1–Ru–N3	89.9(1)	N1–Ru–N4	176.3(2)	Ru–N1–C3	109.8(3)
Cl1–Ru–N4	84.5(1)	N2–Ru–N3	161.6(2)	N1–C3–C4	107.0(4)
Cl2–Ru–N1	89.3(1)	N2–Ru–N4	98.6(2)	C3–C4–N3	109.8(4)
Cl2–Ru–N2	88.2(1)	N3–Ru–N4	99.8(2)	C4–N3–Ru	109.8(3)
Cl2–Ru–N3	88.3(1)	Ru–N2–C1	110.1(3)	Ru–N4–O	175.5(4)
		mer−[$RuBr_3$(Hdien)NO]Br·H_2O (**2**)			
Ru–Br1	2.501(4)	Ru–N4	1.77(3)	C3–C4	1.68(5)
Ru–Br2	2.510(4)	N1–C1	1.48(5)	C4–N3	1.39(5)
Ru–Br3	2.514(4)	C1–C2	1.43(5)	N4–O	1.17(4)
Ru–N1	2.15(3)	C2–N2	1.45(5)		
Ru–N2	2.13(2)	N2–C3	1.71(4)		
Br1–Ru–Br2	90.5(2)	Br2–Ru–N4	94.7(12)	N1–C1–C2	108.7(31)
Br1–Ru–Br3	174.5(2)	Br3–Ru–N1	89.2(7)	C1–C2–N2	106.8(29)
Br1–Ru–N1	85.4(7)	Br3–Ru–N2	93.4(10)	C2–N2–Ru	108.5(22)
Br1–Ru–N2	85.3(10)	Br3–Ru–N4	93.7(9)	C2–N2–C3	111.5(29)
Br1–Ru–N4	91.8(9)	N1–Ru–N2	77.7(13)	Ru–N2–C3	107.0(19)
Br2–Ru–Br3	89.6(2)	N1–Ru–N4	175.7(14)	N2–C3–C4	104.1(23)
Br2–Ru–N1	88.6(10)	N2–Ru–N4	98.1(15)	C3–C4–N3	104.4(26)
Br2–Ru–N2	165.9(8)	Ru–N1–C1	109.9(23)	Ru–N4–O	177.6(28)
		Interatomic bond lengths and angles around the N3			
N3–Br4(A)	3.28(3)	Br4(A)–N3–Br4(B)	109.5(9)	Br4(A)–N3–C4	108.5(20)
N3–Br4(B)	3.33(3)	Br4(A)–N3–O2(C)	125.3(14)	C4–N3–Br(B)	94.6(19)
N3–O2(C)	2.87(3)	Br(B)–N3–O2(C)	101.0(10)	C4–N3–O2(C)	113.1(23)

Key to symmetry oparation; A: $x,y,z-1$; B: $-x+1/2, -y+1, z+1/2-1$; C: $-x,y+1/2, -z+1/2$.

position *trans* to the NO is shorter than the Ru–N2 or Ru–N3 bond in a position *cis* to the NO. However, in **2**, the Ru–N1 in a position *trans* to the NO is longer than Ru–N2 bond in a position *cis* to the NO. It has been reported that in *sym-fac*- and *unsym-fac*-[$RuCl_2$(dien)-NO]I, the bond between the central nitrogen atom of the dien and the Ru (2.106 Å for the *sym-fac* isomer and 2.082 Å for the *unsym-fac* isomer) is shorter than those between the terminal nitrogen atoms and the Ru (2.113 and 2.116 Å for the *sym-fac* isomer and 2.103 and 2.104 Å for the *unsym-fac* isomer), whether the central nitrogen atom is in a position *cis* or *trans* to the NO.[5] Thus, it is concluded that the shortening found in **1** is not caused by the NO.

***trans-mer*-[$RuCl_2$(dien)NO]Y (Y=I or PF_6).** The elemental analysis agreed well with the proposed formula for the complexes. The observed ν(NO) bands indicate that the complexes are {Ru^{II}–NO^+}-type.[1] In the ^{1}H NMR spectrum, multiplet resonance signals due to the methylene protons were observed at δ= 2.99—3.66. Two slightly broad signals at δ=6.14 and 6.20 were assigned to the terminal amine protons. Only one signal due to the central immine proton was observed at δ=7.48. The integrated intensity ratio of these resonances was 8:2:2:1. In the COSY spectrum, the two signals due to the terminal amine protons were correlated with each other. Therefore, these signals were assigned to the axial and equatorial protons. The same correlation was found in the signals due to the methylene protons, although the signals showed a multiplet that was caused by the germinal coupling and overlapping of the signals. In the ^{13}C NMR spectrum, two signals due to the methylene carbons were observed at δ=47.66 and 50.57. The signals were expected to be observed in the three isomers (the *sym-fac*, *trans-mer*, and *cis-mer* isomers; see Scheme 1). Because the signals for the *sym-fac* isomer are observed δ=43.4 and 52.9,[5] the complex **1** seems to be in the *mer* form. However, it could not be decided from the NMR spectra alone whether the complex **1** is the *trans-mer* or the *cis-mer* isomer.

***mer*-[$RuBr_3$(Hdien)NO]Br·H_2O(2).** The elemental analysis agreed well with the proposed formula for the complex. The ν(NO) band shows that the complex is also {Ru^{II}–NO^+}-type.[1] In the ^{1}H NMR spectrum, multiplet resonance signals due to the methylene protons (8H) were observed at δ=2.85—3.51. Four slightly broad resonance signals were observed at δ=

6.07 (**a**), 6.14 (**b**), 6.72 (**c**), and 7.86 (**d**) and the integrated intensity ratio was 1 : 1 : 1 : 3. The signals are obviously different from those of other complexes containing a dien that coordinates as a tridentate ligand. In the ^{13}C NMR spectrum, four signals due to the methylene carbons were observed at δ=36.16 (**e**), 45.39 (**f**), 52.19 (**g**), and 52.45 (**h**), indicating that each of the carbons is in a different environment. The signal at the highest field (δ=36.16) was rather near that (δ=35.89) of a free acidified dien in DMSO-d_6 containing DBr. The COSY and C–H COSY spectra were measured, and the signals could be assigned by tracing the correlations: **a** and **b**, the terminal axial and equatorial amine (N1) protons; **c**, the central imine (N2) proton; **d**, the terminal ammonium (N3) protons; **e**, the methylene carbon (C4) neighboring the terminal ammonium; **f**, the methylene carbon (C1) neighboring the terminal amine; **g**, the methylene carbon (C2) neighboring the central imine; and **h**, the methylene carbon (C3) neighboring the central imine. These observations support the idea that the Hdien ligand coordinates to the ruthenium through one terminal and the central nitrogen atoms as a bidentate ligand and the other terminal nitrogen is present as an ammonium moiety. The signals **a** and **b** became close to each other with increasing temperature to give finally one signal (δ=5.95) above 333 K. These results support the assignment by the 2D NMR measurements. The results obtained from the temperature-varied ^1H NMR measurement suggest there is a hindrance to the ring inversion at room temperature because of the presence of the large uncoordinated moiety. The structure of the complex estimated from the NMR spectra was consistent with that found by this X-ray diffraction.

The preparation in an alkaline medium caused denitrosylation of the starting material, hydrous $RuX_3 \cdot NO$ (X=Cl or Br), to give unidentified products.

The same procedure as used for the synthesis of the chloro complex (**1**) was done for synthesis of the bromo complex under neutral conditions (pH 6.5) with hydrous $RuBr_3 \cdot NO$ as a starting material. Two species were isolated, but reproducibility of the reaction was poor. The species obtained were identified to be *trans-mer-* and *sym-fac*-$[RuBr_2(dien)_2NO]PF_6$ by comparison with the NMR spectra of the corresponding chloro complexes,[5] but X-ray diffraction study is indispensable for correct characterization of the complexes.

On the other hand, the same procedure as used for the synthesis of the bromo complex (**2**) was done for synthesis of the chloro complex under the acidic conditions (pH 2—4) with hydrous $RuCl_3 \cdot NO$ as a starting material, and two species were obtained. These were eluted as a mixture from the first column chromatography, and a further chromatographic separation was done with a longer column (ϕ 2×50 cm) to isolate these species. These were characterized by the NMR spectra. One could be identified to be *trans-mer*-$[RuCl_2(dien)_2NO]I$ and the other, *sym-fac*-$[RuCl_2(dien)_2NO]I$.[5] A chloro complex containing an Hdien ligand was expected, but could not be obtained in the acidic medium. From either the reaction in the acidic medium or the reaction in the neutral medium, *trans-mer*-$[RuCl_2(dien)_2NO]^+$ was obtained. On the other hand, the *sym-fac* isomer was not synthesized in the acidic medium. The reaction in the neutral medium was more appropriate to obtain the *trans-mer* isomer.

These results seem to reflect the difference in the reactivity between hydrous $RuCl_3 \cdot NO$ or hydrous $RuBr_3 \cdot NO$ and dien in this pH range, but the reasons are not clear.

The *cis-mer* isomer was expected to be prepared considering the *trans*-strengthening effect of the NO because the halide ion is a good σ- and π-donor ligand, but the isomer could not be prepared under these preparative conditions.

References

1) F. Bottomley, *Coord. Chem. Rev.*, **26**, 7 (1978).
2) Y. Kamata, T. Kimura, R. Hirota, E. Miki, K. Mizumachi, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **60**, 1343 (1987).
3) Y. Kamata, R. Hirota, E. Miki, K. Mizumachi, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **61**, 594 (1988).
4) H. Tomizawa, K. Harada, E. Miki, K. Mizumachi, T. Ishimori, A. Urushiyama, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **66**, 1658 (1933).
5) Y. Kushi, S. Otoishi, and H. Yoneda, "The 36th Symposium on Coordination Chemistry of Japan," Nagoya, October 1986, Abstr., 3AP04.
6) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, **24**, 351 (1968).
7) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res. (Jpn.)*, **55**, 69 (1979).
8) "International Tables for X-Ray Crystallography," Kynoch, Birmingham, England (1974), Vol. IV, Tables 2.2A and 2.3.1.
9) R. F. Stewart, E. R. Davison, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
10) J. E. Fergusson, C. T. Page, and W. T. Robinson, *Inorg. Chem.*, **15**, 2270 (1976).
11) R. K. Coll, J. E. Fergusson, V. McKee, C. T. Page, W. T. Robinson, and T. S. Keong, *Inorg. Chem.*, **26**, 106 (1987).
12) E. Miki, K. Harada, Y. Kamata, M. Umehara, K. Mizumachi, T. Ishimori, M. Nakahara, M. Tanaka, and T. Nagai, *Polyhedron*, **10**, 583 (1991).
13) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 1420 (1972).
14) J. T. Veal and D. J. Hodgson, *Acta Crystallogr., Sect. B*, **28**, 3525 (1972).
15) H. Nishimura, H. Matsuzawa, T. Togano, M. Mukaida, H. Kakihana, and F. Bottomley, *J. Chem. Soc., Dalton Trans.*, **1990**, 137.
16) J. D. Oliver and D. P. Riley, *Inorg. Chem.*, **23**, 156 (1984).
17) **1** is called *trans-mer* in this paper. The formal name of **1** is (*OC*-6-14)-[*N*-(2-amino-κN-ethyl)-1,2-ethane-

diamine-κ^2N,N']dichloronitrosylruthenium(1+) hexafluorophosphate.

18) Equation of weighted best plane; $14.72(2)X-0.047(6)Y-8.062(6)Z=0.716(6)$.

19) The formal name of **2** is (*OC*-6-32)-tribromo[*N*-(2-ethylammonium)-1, 2-ethanediamine-κ^2N,N']nitrosylruthenium(1+) bromide monohydrate.

20) Equation of weighted best plane; $6.27(1)X+0.58(3)Y-6.083(4)Z=-0.061(5)$.

21) N. V. Ivanova and A. B. Nikol'skii, *Sov. J. Coord. Chem.* (*Engl. Transl.*), **1**, 582 (1976).

22) A. B. Nikol'skii, V. I. Baranovskii, N. V. Ivanova, and O. V. Sizova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **19**, 145 (1974).