Preparation and Characterization of Ethylenediaminetrihalogenonitrosylruthenium(III) Complexes

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A mixture of *mer*- and *fac*-[$RuCl_3$(en)NO], and *mer*-[RuX_3(en)NO] (X=Br or I) were prepared from the corresponding $[RuX_5NO]^{2-}$ (X=Cl, Br, or I) or hydrous RuX_3·NO (X=Cl or Br) and en·2HX (en=ethylenediamine; X=Cl or Br). The crystal and molecular structures of *mer*-[RuX_3(en)NO] (X=Cl, Br, or I) were determined by X-ray diffraction. The crystals were isomorphous; triclinic, with space group $P\bar{1}$. The final R values were 0.0411 for [$RuCl_3$(en)NO], 0.0271 for [$RuBr_3$(en)NO], and 0.0535 for [RuI_3(en)NO]. In these complexes, the three halogeno atoms were in the meridional arrangement and in a position *cis* to the NO. In all of the *mer*-complexes, the *trans*-strengthening effect which is expected to be caused by the NO was not observed for the Ru–N(en) bond. The synthesized complexes were also characterized by IR and NMR spectra.

Coordinated NO^+ influences the formation, reactivity, and structure of $\{RuNO\}^6$-type complexes. This has been explained from the point of view of a weak σ-donor and the strong π-acceptor quality of the NO; specifically, the *trans*-strengthening effect due to the NO is well-known.[1] The nitrosylruthenium(III) complexes containing ammine ligands which show σ-bonding ability on coordination have been extensively studied.[2] Bottomley's attempt to test the σ-bonding contribution to the effect by reinvestigation of the X-ray structural determination of $[Ru(NH_3)_5NO]Cl_3·H_2O$ did not succeed because of technical problems with the structure.[3] Two studies on nitrosylruthenium(III) complexes containing ethylenediamine (which shows σ-bonding ability on coordination) have been published; $[Ru(OH)(en)_2NO]^{2+}$ was synthesized by Werner and Smirnoff in 1920,[4] and $[RuX(en)_2NO]^{2+}$ (X=HClOH, Cl, Br, or I) and [RuX_3(en)NO] (X=Cl or I) by Charronat in 1931.[5] Because these investigations were performed early in the study of nitrosylruthenium(III) chemistry, no detailed investigation of the structures of the complexes was performed. The nitrosylruthenium(III) complexes containing ethylenediamine are suitable for the examination of the σ-bonding contribution of ethylenediamine to the *trans*-strengthening effect. We have prepared *mer*- and *fac*-[$RuCl_3$(en)NO] and *mer*-[RuX_3(en)NO] (X=Br or I), and characterized them using NMR and IR. The structures of *mer*-[RuX_3(en)NO] (X=Cl, Br, or I) have been determined by X-ray diffraction.

Experimental

Measurements. The UV-vis spectra of the complexes in DMSO were measured with a Hitachi U-3410 spectrophotometer. The infrared spectra were measured with JASCO A-202 (4000—400 cm^{-1}), JASCO IR-F (700—200 cm^{-1}), and JEOL JIR-5500 (500—50 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. All the ^{13}C NMR spectra were collected by measuring ^1H complete decoupling.

Synthesis. Mixture of *mer*-(1) and *fac*-[$RuCl_3$(en)NO] (2): An aqueous solution of en·2HCl (en=ethylenediamine) (1.5 mmol in 20 cm^3) was added to an aqueous solution of $K_2[RuCl_5NO]$ (1 mmol in 30 cm^3) or $RuCl_3$·NO·1.5H_2O (1 mmol in 30 cm^3 dilute HCl). The solution was adjusted to pH 6 with an aqueous sodium hydroxide solution, and was heated near the boiling point for 1 h. After heating, the pH had returned to near the initial pH, ca. 3. Adjustment of the pH to 6 was repeated until the pH did not change after heating. The resultant solution was refluxed for 3 h and cooled slowly to deposit browm and red crystals. The crystals were collected by filtration and washed with water and ethanol, then air dried; yield 54%. Attempts to separate the species using chromatographic techniques did not succeed. Thus, the crystals were separated by hand using a needle under a microscope. The separation was difficult since most of the crystals were joined together. From 2 g of the mixture, 0.6 mg of the brown and 0.4 mg of the red crystals were obtained, and only the ^1H and ^{13}C NMR, and IR (KBr disk) spectra were measured. For measuring the COSY and C–H COSY spectra, the mixture was used. Found (mixture): Ru, 35.1; C, 8.09; H, 2.41; N, 13.88; Cl, 35.48%. Calcd for $C_2H_8N_3OCl_3Ru$: Ru, 34.0; C, 8.07; H, 2.71; N, 14.12; Cl, 35.75%. IR (KBr) ν_{NO} at 1860 cm^{-1} for the brown crystals, ν_{NO} at 1860 cm^{-1} for the red crystals.

***mer*-[$RuBr_3$(en)NO] (3): Ethanol Media.** An aqueous solution of en (3 mmol in 5 cm^3) partially neutralized by HBr (pH ca. 8) was added to an ethanol solution of hydrous $RuBr_3$·NO (1.5 mmol in 50 cm^3). After the mixture had been refluxed for 3 h, the solution was filtered hot to remove insoluble materials. The filtrate was concentrated on a rotary evaporator to ca. 10 cm^3, whereupon crude crystals were deposited. The crystals were collected by filtration and washed with water and ethanol, then air dried. An acetonitrile solution of the crystals (50 mg in 20 cm^3) was adsorbed on 10 g of silica gel (Wakogel C-300). After the solvent had been removed from the mixture by an evaporator, the silica gel suspended in CH_2Cl_2 was transferred onto a column of silica gel (Wakogel C-300, ϕ 4×30 cm), and a chromatogram was developed with ethyl acetate. The pink eluate obtained as the only band was evaporated. The obtained reddish brown solid was triturated with water,

filtered, washed with water and ethanol successively, and air dried. The compound was recrystallized from acetonitrile–diethyl ether: yield 44%.

Water Media. The same procedure as the synthesis of $[RuCl_3(en)NO]$ was applied using $K_2[RuBr_5NO]$ or hydrous $RuBr_3 \cdot NO$ (1 mmol) and en·2HBr (1.5 mmol). The reaction product was purified in the same way as in the synthesis in ethanol media by using a column of silica gel (Wakogel C-300, ϕ 4×20 cm): yield 62%. Found: Ru, 24.1; C, 5.89; H, 1.86; N, 9.80%. Calcd for $C_2H_8N_3OBr_3Ru$: Ru, 23.5; C, 5.58; H, 1.87; N, 9.75%. IR ν_{NO} at 1850 (s) and 1870 (s) cm^{-1} (Nujol), and at 1870 (s) cm^{-1} (DMSO), ν_{RuBr} at 230 (br) cm^{-1} (Nujol); UV (DMSO) 18200 (ε/$mol^{-1}\,dm^3\,cm^{-1}$ 63, sh) and 20600 cm^{-1} (ε 120).

***mer*-[RuI$_3$(en)NO] (4):** The compound was prepared in the same way as in the synthesis of $[RuCl_3(en)NO]$ using $K_2[RuI_5NO]$ (1 mmol) and en·2HCl (1.5 mmol). The crude product was purified by the same column chromatography as for **3** using 10 vol% ethyl acetate–dichloromethane as the eluent. The dark reddish brown compound was recrystallized from acetonitrile–diethyl ether: yield 30%. Found: Ru, 17.6; C, 4.43; H, 1.18; N, 7.28; I, 66.31%. Calcd for $C_2H_8N_3OI_3Ru$: Ru, 17.7; C, 4.20; H, 1.41; N, 7.35; I, 66.31%. IR ν_{NO} at 1860 (s) and 1880 (sh) cm^{-1} (Nujol), and at 1860 (s) cm^{-1} (DMSO), ν_{RuI} at 192(w) and 199(w) cm^{-1} (Nujol); UV (DMSO) 17500 (ε/$mol^{-1}\,dm^3\,cm^{-1}$ 208, sh), 21300 cm^{-1} (ε 1390, sh), and 28700 cm^{-1} (ε 7660).

X-Ray Crystal Analysis of *mer*-[RuX$_3$(en)NO] (X=Cl, Br, or I). A crystal of **1** for structure analysis was chosen from the separated brown crystals. To obtain crystal suitable for structure determination, **3** or **4** (0.1 g) was dissolved in acetonitrile (30 cm^3) and the solution was allowed to evaporate at room temperature. Several days after, dark red (**3**) or black (**4**) plate crystals were obtained.

For crystals of **1**, **3**, or **4**, a similar method of data collection and of refinement was applied. Crystal and intensity collection data are shown in Table 1. Preliminary Weissenberg photographs taken with Cu $K\alpha$ radiation (λ= 1.54184 Å) showed **1**, **3**, and **4** to be triclinic. The crystals were transferred to a 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 least-squares refinement using 20 reflections ($20° \leqq 2\theta \leqq 25°$). For weak reflections, measurements were repeated up to four times. Crystal stability was monitored by recording three standard reflections every 100 reflections, and no significant variations were observed. For structure determination and refinement, the intensity data of unique reflections with $|F| \geqq 3\sigma(|F|)$ 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 FACOM M-760 computer by using the UNICS III Program System[7] at the Computer Center of Rikkyo University. The structures were solved by the heavy-atom method and refined by the full-matrix least-squares method. For **1**, hydrogen atoms were observed in difference Fourier syntheses except one (H Nl) which was placed at the calculated position. All of them were included in the refinement. For **3**, all hydrogen atoms were observed in difference Fourier syntheses and were included in the refinement. For **4**, only two hydrogen atoms (H Cl and H′ Cl) were observed in difference Fourier syntheses. The others were placed at the calculated positions, and were not included in the refinement. The final R values were 0.0411 for **1**, 0.0271 for **3**, and 0.0535 for **4** with anisotropic temperature factors except hydrogen atoms and with isotropic factors for hydrogen atoms. The atomic scattering factors were taken from Ref. 8 for non-hydrogen atoms and from Ref. 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. 66016 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Crystal and Molecular Structures. The crystals of **1**, **3**, and **4** were isomorphous to each other as shown in Table 1 and the lattice constants were similar but increased in the order of Cl, Br, and I. In each complex, three halogen atoms are in the meridional arrangement and in a position *cis* to the NO. The molecular structure of *mer*-$[RuBr_3(en)NO]$ is shown in Fig. 1. Table 3 shows selected intramolecular bond lengths and angles of the complexes. Figure 2 shows the crystal structure of *mer*-$[RuBr_3(en)NO]$, and shows that two kinds of complexes exist in the crystal lattice. Because the space group is $P\bar{1}$ but the symmetry center does not exist on the atoms, the ethylenediamine ring in one of the complexes has a δ gauche conformation and that in another complex has a λ gauche conformation. The same conformation for the ethylenediamine ring was also observed in the chloro and iodo complexes.

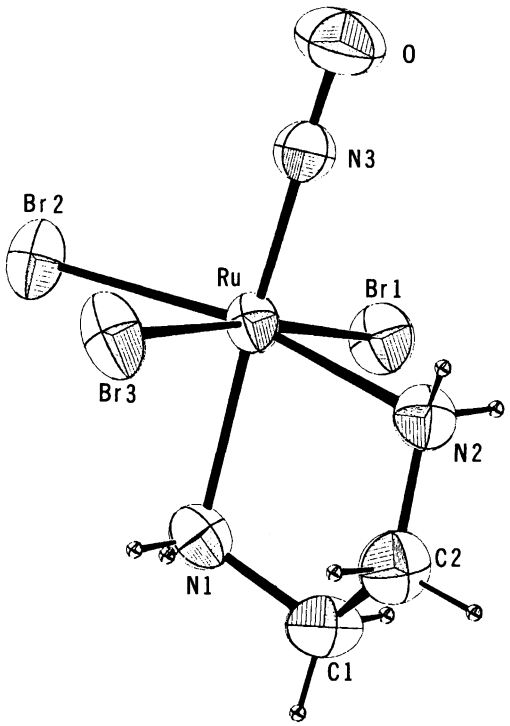

Fig. 1. ORTEP drawing and atomic numbering scheme of *mer*-$[RuBr_3(en)NO]$.

Table 1. Crystal and Intensity Collection Data

Parameter	[$RuCl_3$(en)NO] (**1**)	[$RuBr_3$(en)NO] (**3**)	[RuI_3(en)NO] (**4**)
Formula	$RuCl_3ON_3C_2H_8$	$RuBr_3ON_3C_2H_8$	$I_3RuON_3C_2H_8$
MW	297.53	430.89	571.89
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	6.638(6)	6.918(3)	7.326(1)
b/Å	11.389(7)	11.791(3)	12.394(2)
c/Å	6.853(3)	6.524(4)	7.284(2)
α/°	95.69(5)	93.74(3)	90.19(2)
β/°	112.90(7)	115.36(4)	117.74(2)
γ/°	101.70(7)	101.75(3)	102.56(1)
V/Å^3	436.1(6)	487.1(4)	567.1(2)
Z	2	2	2
D_m/g cm^{-3}	2.26	2.94	3.35
D_c/g cm^{-3}	2.27	2.94	3.35
Crystal size/mm	0.12×0.10×0.03	0.40×0.40×0.10	0.48×0.20×0.06
μ(Mo $K\alpha$)/cm^{-1}	26.36	137.23	94.00
F(000)	288	396	504
Scan mode	ω–2θ	$\omega(2\theta \leqq 25°)$ ω–$2\theta(25° \leqq 2\theta \leqq 55°)$	ω–2θ
Scan width	1.15+0.40 tan θ	1.20+0.50 tan θ	1.15+0.45 tan θ
No. of reflections collected	2187	2125	2817
No. of reflections with $\|F\| \geqq 3\sigma(\|F\|)$	1702	1788	2633
R[a]	0.0411	0.0271	0.0535
R_w[b]	0.0506[c]	0.0294[d]	0.0681[c]

a) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. b) $Rw=(\Sigma w(||F_o|-|F_c||)^2/\Sigma w|F_o|^2)^{1/2}$. c) $w=1$. d) $w=1/|\Delta F|^2=a|F_o|^2+b|F_o|+c$ ($a=0.0012$, $b=-0.07$, $c=1.7$).

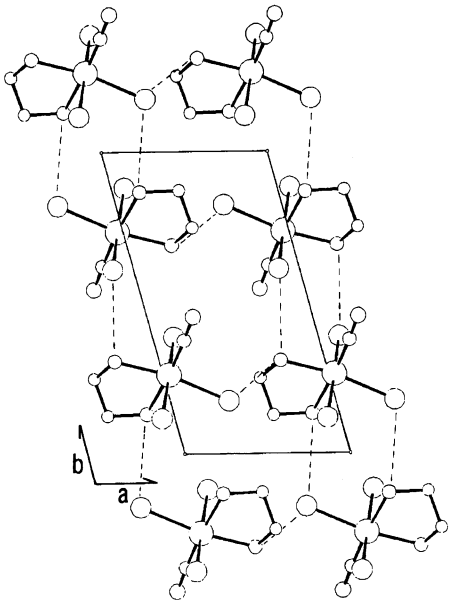

Fig. 2. The crystal structure of *mer*-[$RuBr_3$(en)NO] projected along the c axis. The dotted lines indicate hydrogen bonds.

In all of the crystals, hydrogen bonds were observed between the halogeno ligands and amine protons as shown in Fig. 2. All of the Ru–X bond lengths are typical of those found in other ruthenium(II) complexes containing halogeno ligands.[10—14] The NO is essentially linear 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,[12—19] showing that NO formally coordinates to ruthenium(II) as NO^+. With increasing atomic number of the halogen, the linearities of the Ru–N–O and of the Nl–Ru–NO bond angles increased. The complexes are of a slightly-distorted octahedron. In all of the complexes, the Ru atom is displaced toward the NO group out of the best plane consisting of the three halogen and the nitrogen(N2) atoms,[20] and also the displacement decreases in the order of Cl, Br, and I; 0.176(2), 0.1518(7), and 0.106(2) Å. These distortions may be attributed to the steric hindrance between the bulky Ru–NO bond orbital and the halogeno ligands. Because the larger the halogen is the longer the Ru–X bond length is, the distortion is eased in the order of Cl, Br, and I. In fact, the average interatomic distance between the nitrogen atom of the NO and the halogen atoms becomes larger; 3.05 Å for X=Cl, 3.15 Å for X=Br, and 3.27 Å for X=I. The ethylenediamine rings have typical bond lengths and angles as observed in other ruthenium complexes.[21,22] The bond length of the Ru–N1 was longer than that of the Ru–N2, though the lengthening was not apparent for X=Cl and Br when the standard deviations were considered. Such a *trans* lengthening was enhanced in the order of Cl, Br, and I. X-ray crystal analysis of $A_2[RuCl_5NO]$ (A=NH_4 or K) by Veal and Hodgson shows that the Ru–Cl (*trans* to the NO) bond length is shorter than the Ru–Cl (*cis* to the NO) bond length,[15,16] which is

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

Atom	x	y	z	B_{eq}[a)]/Å^2
		[$RuCl_3$(en)NO] (**1**)		
Ru	0.0347(1)	0.2652(1)	0.1284(1)	2.2
Cl1	−0.0908(4)	0.1247(2)	0.3229(4)	3.2
Cl2	0.3386(4)	0.1760(2)	0.1789(4)	3.3
Cl3	0.1339(4)	0.3841(2)	−0.1141(4)	3.5
O	0.267(1)	0.4726(6)	0.498(1)	4.7
N1	−0.161(1)	0.1314(6)	−0.167(1)	2.5
N2	−0.273(1)	0.3135(7)	0.027(1)	2.8
N3	0.179(1)	0.3857(6)	0.358(1)	2.6
C1	−0.405(2)	0.1269(8)	−0.248(2)	3.2
C2	−0.422(2)	0.2568(8)	−0.212(2)	3.2
		[$RuBr_3$(en)NO] (**3**)		
Ru	0.03544(7)	0.26226(3)	0.11193(7)	2.4
Br1	−0.07760(9)	0.11799(5)	0.32013(9)	3.2
Br2	0.35276(9)	0.17490(5)	0.1725(1)	3.5
Br3	0.1265(1)	0.38751(5)	−0.1361(1)	3.9
O	0.2749(9)	0.4535(4)	0.4759(8)	5.3
N1	−0.1634(8)	0.1326(4)	−0.1716(8)	2.9
N2	−0.2675(8)	0.3084(4)	0.0081(8)	2.9
N3	0.1833(7)	0.3759(4)	0.3356(7)	2.9
C1	−0.402(1)	0.1278(5)	−0.246(1)	3.6
C2	−0.421(1)	0.2502(6)	−0.221(1)	3.7
		[RuI_3(en)NO] (**4**)		
Ru	0.0345(2)	0.2619(1)	0.0838(2)	2.1
I1	−0.0628(2)	0.1147(1)	0.3186(2)	2.8
I2	0.3645(2)	0.1753(1)	0.1564(2)	3.3
I3	0.1167(2)	0.3966(1)	−0.1764(2)	3.9
O	0.295(2)	0.430(1)	0.439(2)	5.2
N1	−0.169(2)	0.138(1)	−0.183(2)	2.8
N2	−0.260(2)	0.302(1)	−0.023(2)	2.8
N3	0.191(2)	0.363(1)	0.298(2)	2.8
C1	−0.395(3)	0.132(2)	−0.250(3)	3.3
C2	−0.419(3)	0.247(2)	−0.239(3)	3.6

a) $B_{eq}=4/3\sum_i\sum_j B_{ij}a_i a_j$.

explained by differences in the Cl^- and NO^+ σ-bonding ability ($Cl^- > NO^+$) on the basis of an MO calculation for $[MnCl(CO)_5]$.[23] The LCAO MO studies on RuX_5NO-type complexes (X=H_2O, NH_3, Cl^-, or CN^-) by Nikol'skii et al.[24,25] show that the Ru–X (*trans* to the NO) bond is strengthened compared with the Ru–X (*cis* to the NO) bond, and that the difference in the strength of the former and the latter is due to both σ-bonding and π-bonding effects, though the σ-effect is the most important. Thus, the *trans*-strengthening effect is expected to be observed for the bonds between the Ru and ethylenediamine which behaves as a σ-donor on coordination. However, the effect was not observable in this series. This result may indicate that the *trans*-strengthening effect is not found when a ligand having only σ-donor ability coordinates in *trans* to the NO. The longer Ru–N1 bond length for **4** can not be explained without taking steric effects into consideration. As each of the NH_2 groups has a hydrogen atom which was found to be close to the halogeno ligands without distortion in the ring of en, this phenomenon may be caused by a steric effect, though it is not so strong.

***mer*- (1) and *fac*-[$RuCl_3$(en)No] (2).** Two kinds of the crystals were suspected to be a mixture of two species although the elemental analysis agreed well with the proposed formula for the complex.

The ν(NO) band of **1** or **2** was observed at 1860 cm^{-1}, indicating a Ru^{II}–NO^+-type complex.[1] The ^1H and ^{13}C NMR spectra were measured for **1** and **2**. For **1**, triplet signals due to methylene protons of the ethylenediamine ligand were observed at δ=2.86 and 2.94, and slightly broad singlet signals due to amine protons of the ethylenediamine ligand at δ=5.91 and 6.09. The integrated intensity ratio of the four resonances was 1 : 1 : 1 : 1. Two resonance signals due to methylene carbons of the ethylenediamine ligand were observed at δ=45.16 and 45.42. The NMR data indicated that **1** is *mer*-[$RuCl_3$(en)NO] in which the three chlorines are in a meridional arrangement as shown by the X-ray crystal structure analysis of **1**. Complex **2** also showed two resonance signals due to the methylene protons at δ=2.55 and 2.94, and due to the amine protons at δ=5.57 and 6.21 respectively. The integrated intensity ratio of the four resonances was 1 : 1 : 1 : 1. However, only one resonance signal due to the methylene carbon was observed at δ=47.04. The COSY and C–H COSY spectra for the mixture of **1** and **2** were measured for further characterization. The correlations between the signals due to the *mer* complex(**1**) observed on both the COSY and C–H COSY spectra agreed with those expected from the structure. All of the signals due to **2**, δ=2.55, 2.94, 5.57, and 6.21, correlated to each other in the COSY spectrum, and the signals due to the methylene protons, δ=2.55 and 2.94, were correlated with the signal due to the methylene carbon, δ=47.04, in the C–H COSY spectrum. These data indicate that the two kinds of methylene protons which are linked to only one kind of carbon are in different environments as are the two amine protons. The NMR data indicate that **2** is *fac*-[$RuCl_3$(en)NO].

The COSY and H–C COSY spectra showed that the fac isomer has nonequivalent geminal protons in the methylene protons and in the amine protons[26] although the mer isomer does not. It has been reported that the resonance signals due to the methylene protons of *N*-deuterated tris(ethylenediamine)ruthenium(II) ion shows a multiplet,[27] and that it is caused by geminal coupling between the axial and equatorial protons in the methylene protons.[28] If the same analysis can be applied to the present isomers, geminal coupling is expected to be observed in the resonance signals due to the methylene protons of the ethylenediamine ligand even in the mer isomer. However, this coupling was not observed in **1**, **3**, or **4**. This suggests that the conformation of the ethylenediamine ring in the complexes is

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

		[$RuCl_3$(en)NO] (**1**)			
Ru–N1	2.094(6)	Ru–Cl2	2.364(3)	C2–N2	1.471(11)
Ru–N2	2.092(9)	Ru–C13	2.375(3)	N3–O	1.154(9)
Ru–N3	1.727(6)	N1–C1	1.486(13)		
Ru–Cl1	2.356(3)	C1–C2	1.509(13)		
N1–Ru–N2	80.3(3)	N2–Ru–Cl1	89.7(3)	Ru–N1–C1	111.0(6)
N1–Ru–N3	173.9(3)	N2–Ru–C12	168.1(2)	N1–C1–C2	107.5(7)
N1–Ru–C11	86.5(2)	N2–Ru–C13	89.7(3)	C1–C2–N2	107.3(8)
N1–Ru–C12	87.8(2)	Cl1–Ru–C12	88.6(1)	C2–N2–Ru	110.9(7)
N1–Ru–C13	85.3(2)	Cl1–Ru–C13	171.83(7)	Ru–N3–O	174.1(7)
N2–Ru–N3	94.5(3)	C12–Ru–C13	90.32(1)		
		[$RuBr_3$(en)NO] (**3**)			
Ru–N1	2.115(4)	Ru–Br2	2.500(1)	C2–N2	1.482(7)
Ru–N2	2.105(5)	Ru–Br3	2.516(1)	N3–O	1.136(6)
Ru–N3	1.738(5)	N1–C1	1.488(9)		
Ru–Br1	2.504(1)	C1–C2	1.48(1)		
N1–Ru–N2	80.1(2)	N2–Ru–Br1	90.3(2)	Ru–N1–C1	110.2(4)
N1–Ru–N3	175.2(2)	N2–Ru–Br2	168.7(2)	N1–C1–C2	107.9(5)
N1–Ru–Br1	86.7(2)	N2–Ru–Br3	89.5(2)	C1–C2–N2	108.1(5)
N1–Ru–Br2	88.6(2)	Br1–Ru–Br2	88.51(4)	C2–N2–Ru	110.4(5)
N1–Ru–Br3	86.5(2)	Br1–Ru–Br3	173.14(2)	Ru–N3–O	176.9(5)
N2–Ru–N3	95.5(2)	Br2–Ru–Br3	90.37(4)		
		[RuI_3(en)NO] (**4**)			
Ru–N1	2.157(15)	Ru–I2	2.687(2)	C2–N2	1.496(25)
Ru–N2	2.102(15)	Ru–I3	2.719(2)	N3–O	1.150(22)
Ru–N3	1.736(15)	N1–C1	1.477(25)		
Ru–I1	2.712(2)	C1–C2	1.487(28)		
N1–Ru–N2	78.6(6)	N2–Ru–I1	90.3(4)	Ru–N1–C1	110.6(1.1)
N1–Ru–N3	178.0(6)	N2–Ru–I2	168.2(4)	N1–C1–C2	107.8(1.6)
N1–Ru–I1	87.5(4)	N2–Ru–I3	89.5(4)	C1–C2–N2	107.1(1.6)
N1–Ru–I2	89.7(4)	I1–Ru–I2	88.48(5)	C2–N2–Ru	112.2(1.1)
N1–Ru–I3	88.1(4)	I1–Ru–I3	175.58(7)	Ru–N3–O	179.4(1.5)
N2–Ru–N3	99.5(7)	I2–Ru–I3	90.81(6)		

easily inverted at room temperture. Therefore, no geminal coupling between the axial and equatorial protons was observed. In the $\{RuNO\}^6$-type complexes, multiplicity of the bond exists not only in the N–O, but in the Ru–NO.[1] Therefore, magnetic anisotropy of the complex may exist along the Ru–NO axis. Each proton of ethylenediamine in the *fac* isomer is, as an average position, on the up or down side of the plane which contains the Ru and is at right angles to the Ru–N–O axis; thus each proton may be influenced strongly by magnetic anisotropy. On the other hand, for the *mer* isomer, the influence may be very weak for the protons because all of the protons lie on the down side of the plane.

***mer*-[$RuBr_3$(en)NO] (3).** The elemental analysis agreed well with the proposed formula for the complex. The ν_{NO} band in Nujol mull split into 1850 and 1870 cm^{-1}, but no splitting was observed in a DMSO solution. The same observation has been reported only in the study of $[Ru(NH_3)_5NO]Cl\cdot H_2O$.[3] In the study, it was explained to be due to the environment of the NO with respect to the counter anion. However, the same explanation can not apply to **3** since it does not have a counter ion. The splitting showed some difference in the environment of the NO in the solid state but the difference was not made clear from the X-ray crystal structure analysis. Triplet signals due to methylene protons of the ethylenediamine ligand were observed at $\delta=2.94$ and 3.06 with the $^3J_{HH}=5.5$ Hz. Two slightly broad singlet signals at $\delta=5.80$ and 6.00 were assigned to amine protons of the ethylenediamine ligand. Two resonance signals due to methylene carbons of the ethylenediamine ligand were observed at $\delta=45.58$ and 46.34. These results indicate that the complex is of the *mer*-type.

***mer*-[RuI_3(en)NO] (4).** The elemental analysis agreed well with the proposed formula for the complex. The NO stretching band in Nujol mull split into 1860 and 1880 cm^{-1}, but no splitting was observed in a DMSO solution. This result was the same as in

mer-[$RuBr_3$(en)NO]. Triplet signals due to methylene protons of the ethylenediamine ligand were observed at δ=2.92 and 3.08 with the $^3J_{HH}$=5.5 Hz. Two slightly broad singlet signals at δ=5.59 and 5.97 were assigned to amine protons of the ethylenediamine ligand. Two resonance signals due to methylene carbons of the ethylenediamine ligand were observed at δ=45.88 and 48.52. These results indicate that the complex is of the *mer*-type.

In the *mer*-[RuX_3(en)NO] (X=Cl, Br, or I), the ν_{NO} did not show significant variation with X because the halogeno ligands are located in a position *cis* to the NO. One of the resonance signals due to the methylene carbons shifted to a lower field in the order of Cl, Br, and I (δ=45.42 for X=Cl, 46.34 for X=Br, and 48.52 for X=I), while another signal hardly shifted (δ=45.16 for X=Cl, 45.58 for X=Br, and 45.88 for X=I). From these results, the former can be assigned to the carbon bound directly to the nitrogen which is situated in a position *cis* to the NO, and the latter can be assigned to another carbon.

The structures of [RuX_3(en)NO] (X=Cl, Br, or I) were clarified by the present study. For X=Cl, both the *mer* and *fac* isomers were obtained, while for X=Br and I, only the *mer* isomer was obtained. The NO^+ group is a weak σ-donor and a strong π-acceptor, and σ- and π-donor abilities of the halogeno ligands increase in the order of $Cl^- < Br^- < I^-$.[29] The *fac* isomers of the bromo and iodo complexes were expected to be prepared considering the electronic interaction of the NO^+ with the halogeno ligand along the ON–Ru–X axis. However, the *fac* isomers could not be prepared for X=Br and I. Thus, for X=Br and I, there may be some other advantage (perhaps steric) that dominates over the electronic advantage which is expected for the *fac* arrangement.

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