Preparation and Characterization of *trans*- and *cis*-Anionobis(ethylenediamine)nitrosylruthenium(II) Complexes

Hiroshi TOMIZAWA,* Eiichi MIKI,* Kunihiko MIZUMACHI, and Tatsujiro ISHIMORI
Department of Chemistry, College of Science, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171

(Received December 20, 1993)

In this study *trans*-$[Ru(OH)(en)_2NO]^{2+}$ (en=ethylenediamine) as well as *trans*- and *cis*-$[RuX(en)_2NO]^{n+}$ (X=Cl, Br, I, OAc (acetate), and NCS where n=2; X=H_2O where n=3) were prepared. The complexes were characterized by IR, NMR, and UV-vis spectra. Although a decrease in the wave number of ν(NO) along with an increase in the π-donor ability of X was observed in the *trans* isomers, it was not observed in the *cis* isomers. In the ^{1}H NMR spectra of all the complexes, the resonance signals due to methylene and the amine protons of the en were influenced by the magnetic anisotropy caused by the RuNO group. Two kinds of isomerization reactions were found to be involved in the preparation of the complexes: One was accompanied by a substitution reaction from OH^- to X^-; the other occurred after the substitution reaction. Moreover, ligand X was substituted immediately by OH^- when sodium hydroxide was added to an aqueous solution of the complex; *cis* to *trans* isomerization then occurred for the *cis* isomer.

It is well known that coordinated NO^+ influences the synthesis, reactivity, and structure of $\{Ru^{II}\text{–}NO^+\}$-type complexes, which has been explained on the basis of a *trans*-strengthening effect due to the strong π-acceptor and the weak σ-donor abilities of the NO.[1—3] The $\{Ru^{II}\text{–}NO^+\}$-type complexes containing ammine ligands, which show a σ-donor ability on coordination, have been extensively studied.[4] Ethylenediamine (en) is a very common bidentate ligand which also shows only a σ-donor ability on coordination. However, there has been no study concerning $\{Ru^{II}\text{–}NO^+\}$-type complexes containing ethylenediamine, except for two classical studies.[5,6] We recently reported on the preparation and structures of mono(ethylenediamine)-type complexes; the *trans*-strengthening effect was not observed for the Ru–N(en) bond in *mer*-$[RuX_3(en)NO]$ (X=Cl, Br, and I).[7] It has been expected that further information concerning the effect of the NO on the synthesis, reactivity, and structure of $\{Ru^{II}\text{–}NO^+\}$-type complexes can be obtained from bis(ethylenediamine)-type complexes, *trans*- and *cis*-$[RuX(en)_2NO]^{n+}$, by changing the X. We have thus attempted to systematically prepare, *trans*-$[Ru(OH)(en)_2NO]^{2+}$ and six pairs of the geometrical isomers, *trans*- and *cis*-$[RuX(en)_2NO]^{n+}$ (X=Cl, Br, I, OAc, and NCS where n=2; X=H_2O where n=3). The complexes were characterized by using IR, NMR, and UV-vis spectra.

Experimental

Measurements. The infrared spectra were measured by the Nujol mull method 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 ^{1}H, ^{13}C, ^{14}N, 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, except for the ^{14}N NMR spectrum. For the ^{14}N NMR measurements, H_2O–D_2O (the volumetric ratio 2 : 1) was used as a solvent, and the spectra were referred to external CH_3NO_2. The UV-vis spectra of the complexes were measured using a Hitachi U-3410 spectrometer. For the UV-vis spectrum measurements, except for **2**, **4**, **5**, and **14**, the counter anions were exchanged to Cl^- by using an anion-exchange column (MCI GEL, Cl^- form). All of the spectra were measured in water, except for **13**, the spectrum of which was measured in 6 mol dm^{-3} HCl.

Materials. $[RuX_3(en)NO]$ (X=Cl or Br)[7] and *cis*-$[RuX_2(en)_2]Cl\cdot H_2O$ (X=Cl or Br)[8] were prepared according to methods described in the literature. The other reagents were used of special grade.

Preparation of Compounds. ***trans*-[Ru(OH)(en)$_2$NO]I$_2$ (1):** An aqueous solution of ethylenediamine (1.5 mmol in 10 cm^3) was added to a suspension of the mixture of *mer*- and *fac*-$[RuCl_3(en)NO]$ (1 mmol in 30 cm^3 of water). After the mixture was boiled with stirring for 30 min, the complex was dissolved and the color of the solution changed from dark orange to pale yellow. After the solution was concentrated to ca. 5 cm^3 and cooled, an excess of NaI was added to give yellow crystals. They were collected by filtration and washed with cold water and ethanol successively, and then air dried: yield, 78%. Found: Ru, 20.0; C, 9.22; H, 3.43; N, 13.59%. Calcd for $C_4H_{17}N_5OI_2Ru$: Ru, 19.4; C, 9.20; H, 3.26; N, 13.41%. UV 24400 (sh, ε/mol^{-1} dm^3 cm^{-1} 33.6), 30000 (ε 178), and 41200 cm^{-1} (ε 3820).

***trans*-(2) and *cis*-[RuCl(en)$_2$NO]X$'_2$ (3) (X$'$=Cl (2) and I (3)): Preparation from 1;** **1** (1 mmol) dissolved in 50 cm^3 of 1 mol dm^{-3} HCl was refluxed for 5 h, and was then evaporated up on a rotary evaporator. The crude product was dissolved in 100 cm^3 of water and charged on a cation exchange column (ϕ 4×70 cm) of SP-Sephadex C-25 (H^+ form). The adsorbed bands were separated into two bands by elution with 0.3 mol dm^{-3} HCl. The first yellow band was concentrated on a rotary evaporator to ca. 10 cm^3; yellow crystals (**2**) were precipitated upon adding ethanol. The precipitate was collected by filtration, washed with ethanol, and air dried: yield, 53%. The second band was evaporated up on a rotary evaporator to remove HCl. After the resultant solid was dissolved in a minimum amount of water, an excess of NaI was added to the solution to deposit orange crystals (**3**). The crystals were collected by filtration, washed with ethanol, and air dried: yield 40%.

Selective Preparation of 2 from 1; **1** (1 mmol) dissolved in 30 cm^3 of 6 mol dm^{-3} HCl was heated at ca. 80 °C for 5 min, and was evaporated up on a rotary evaporator. The same column chromatography and precipitation procedures as those used for **2** were applied. Two bands were collected separately by the elution, and **2** was obtained from the first yellow band: yield, 63%. The second band was identified as **1** by its UV spectrum.

Selective Preparation of 3 from *cis*-[RuCl$_2$(en)$_2$]Cl·H$_2$O; *cis*-[RuCl$_2$(en)$_2$]Cl·H$_2$O (1 mmol) was dissolved in 50 cm^3 of 1 mol dm^{-3} HCl, and NO gas was bubbled through the solution with stirring for 3 h at room temperature. The reaction apparatus was deaerated with N$_2$ for 30 min both before and after nitrosylation. The same column chromatography and crystallization procedures as those used for **3** were applied: yield, 97%. Found for **2**: Ru, 28.4; C, 13.35; H, 4.38; N, 19.61%. Calcd for C$_4$H$_{16}$N$_5$OCl$_3$Ru: Ru, 28.3; C, 13.43; H, 4.51; N, 19.58%. Found for **3**: Ru, 18.2; C, 9.33; H, 2.97; N, 13.35%. Calcd for C$_4$H$_{16}$N$_5$OClI$_2$Ru: Ru, 18.7; C, 8.89; H, 2.98; N, 12.96%. UV for **2** 22700 (ε/mol^{-1} dm^3 cm^{-1} 19.9), 30000 (sh, ε 62.2), and 38900 cm^{-1} (ε 3760). UV for **3** 20500 (ε/mol^{-1} dm^3 cm^{-1} 18.4), 29200 (ε 131), and 40800 cm^{-1} (ε 1460).

***trans*-(4) and *cis*-[RuBr(en)$_2$NO]Br$_2$ (5): Preparation from *mer*-[RuBr$_3$(en)NO];** Ethylenediamine (1 mmol) was added to *mer*-[RuBr$_3$(en)NO] (1 mmol) dissolved in 100 cm^3 of hot CH$_3$CN. After the solution was refluxed for 3 h, a yellowish-brown precipitate was deposited. The crude product was collected by filtration and air dried. The same column chromatography as that used for the separation of **2** and **3** was carried out using 0.3 mol dm^{-3} HBr as an eluent to give two bands. From the bands, **4** and **5** were obtained in the elution order by the same procedure as that used for **2**: yield, 6% (**4**) and 20% (**5**).

Compounds **4** and **5** were also prepared by treating **1** with HBr instead of HCl in the same way as that in the syntheses of **2** and **3** from **1**: yield, 43% (**4**) and 40% (**5**). The same selective preparations as that used for **2** and **3** were also carried out for **4** using **1** and for **5** using *cis*-[RuBr$_2$(en)$_2$]Br·H$_2$O in HBr, respectively: yield, 85% (**4**) and 91% (**5**). Found for **4**: Ru, 21.0; C, 10.38; H, 3.29; N, 14.34; Br, 48.75%. Found for **5**: Ru, 20.9; C, 9.94; H, 3.45; N, 14.28; Br, 48.68%. Calcd for C$_4$H$_{16}$N$_5$OBr$_3$Ru: Ru, 20.6; C, 9.78; H, 3.26; N, 14.26; Br, 48.82%. UV for **4** 22200 (sh, ε/mol^{-1} dm^3 cm^{-1} 31.2), 28600 (sh, ε 218), and 34900 cm^{-1} (ε 3640). UV for **5** 20400 (sh, ε/mol^{-1} dm^3 cm^{-1} 28.6), 28500 (ε 191), and 37400 cm^{-1} (ε 1000).

***trans*-[RuI(en)$_2$NO]I$_2$ (6):** After **1** (0.2 mmol) dissolved in 2 mol dm^{-3} HI (20 cm^3) was stirred for 1 h at room temperature, the color changed from yellow to yellowish-orange. The solution was concentrated on a rotary evaporator to ca. 10 cm^3. Ethanol (200 cm^3) was added to the solution, which was then kept overnight in a refrigerator. A yellowish-brown precipitate was collected by filtration, washed with ethanol, and then air dried. A similar chromatographic procedure to that used for **2** was applied to the purification using a column (Na$^+$ form) and 0.3 mol dm^{-3} NaI as an eluent. Only one band was observed. Yellowish-brown crystals were obtained by concentrating the eluate: yield, 67%. Found: Ru, 16.3; C, 7.55; H, 2.43; N, 11.02; I, 60.14%. Calcd for C$_4$H$_{16}$N$_5$OI$_3$Ru: Ru, 16.0; C, 7.59; H, 2.53; N, 11.08; I, 60.28%. UV 23800 (sh, ε/mol^{-1} dm^3 cm^{-1} 399), 29300 (ε 2780), and 40800 cm^{-1} (ε 3530).

***cis*-[RuI(en)$_2$NO]I$_2$ (7):** The compound was prepared by refluxing the same reaction solution as that used for the preparation of **6** for 3 h, and subsequent by purification in the same way as that used for **6** to give dark-brown crystals: yield, 54%. Found: Ru, 16.5; C, 7.61; H, 2.49; N, 11.06; I, 60.26%. Calcd for C$_4$H$_{16}$N$_5$OI$_3$Ru: Ru, 16.0; C, 7.59; H, 2.53; N, 11.08; I, 60.28%. UV 26300 (sh, ε/mol^{-1} dm^3 cm^{-1} 390), 31700 (sh, ε 1270), and 45200 cm^{-1} (ε 25000).

***trans*-[Ru(OAc)(en)$_2$NO]I$_2$·2H$_2$O (OAc=acetate) (8):** A mixture of **1** (0.4 mmol) and sodium acetate (4 mmol) in 50 vol% aqueous acetic acid (40 cm^3) was refluxed for 3 h. The resultant solution was diluted with water to ca. 200 cm^3, and charged on a cation exchange column of SP-Sephadex C-25 (ϕ 4×70 cm, H$^+$ form). The adsorbed band was separated into two bands by elution with 0.3 mol dm^{-3} NaCl, which was adjusted to pH 4 with acetic acid. The first band was collected, and concentrated on a rotary evaporator until NaCl was deposited. Ethanol was added to the solution for further deposition of NaCl; it was then removed by filtration. The removal of NaCl was repeated until it was not deposited in ca. 5 cm^3 of the solution; the solution was then evaporated up. The resultant solid was dissolved in a minimum amount of water, and an excess of NaI was added upon cooling to give yellow crystals, which were collected by filtration, washed with cold water, ethanol successively, and air dried: yield, 30%. Found: Ru, 17.0; C, 12.23; H, 3.72; N, 11.25; I, 45.05; H$_2$O, 6.0%. Calcd for C$_6$H$_{23}$N$_5$O$_5$I$_2$Ru: Ru, 16.8; C, 12.01; H, 3.86; N, 11.64; I, 42.30; H$_2$O, 5.9%. UV 23400 (ε/mol^{-1} dm^3 cm^{-1} 20.5), 33300 (sh, ε 104), and 43000 cm^{-1} (ε 3860). From the second band, **1** was recovered.

***cis*-[Ru(OAc)(en)$_2$NO]I$_2$ (9):** A mixture of solid **5** (1 mmol) and solid silver acetate (3.6 mmol) was ground in an agate mortar with a pestle for 1 h; the mixture then became paste for hygroscopicity of the mixture. About 50 cm^3 of water was added to the paste and the AgBr which formed was removed by filtration; the filtrate was loaded on the same cation exchange column as that used for the preparation of **8**. The same column chromatography, removal of NaCl, and crystallization procedures as those used for the preparation of **8** were applied. From the first band, **1** was recovered. From the second orange band, orange crystals were obtained: yield, 30%. Found: Ru, 18.0; C, 12.52; H, 3.47; N, 12.38%. Calcd for C$_6$H$_{19}$N$_5$O$_3$I$_2$Ru: Ru, 17.9; C, 12.38; H, 3.64; N, 12.03%. UV 20900 (ε/mol^{-1} dm^3 cm^{-1} 26.9), 31500 (ε 140), and 45000 cm^{-1} (ε 2500).

***trans*-[Ru(NCS)(en)$_2$NO]X$'_2$ (X$'$=NCS (10) or I (11)):** A mixture of **2** (0.5 mmol) and NaNCS (5 mmol) in 40 cm^3 of water was refluxed for 2 h. The resultant solution was diluted with water to ca. 200 cm^3, loaded on the same cation exchange column as used for the preparation of **8**, and separated using 0.3 mol dm^{-3} NaNCS as an eluent. The yellow eluate collected as the major band was concentrated on a rotary evaporator to ca. 10 cm^3 to give yellowish-orange crystals (**10**). The crystals were collected by filtration, washed with ethanol, and air dried: yield, 90%. The iodide (**11**) was prepared to clearly distinguish the coordinated thiocyanate ion with the uncoordinated thiocyanate ion in the IR and NMR measurements. The iodide was obtained by adding an excess of NaI to a solution of the corresponding chloride, which was obtained from **10** by exchanging the counter anion through the column (MCI GEL

ϕ 1×10 cm, Cl$^-$ form); the yield was 67%. Found for **10**: C, 19.76; H, 3.80; N, 26.12%. Calcd for $C_7H_{16}N_8OS_3Ru$: C, 19.74; H, 3.78; N, 26.31%. Found for **11**: Ru, 17.8; C, 10.60; H, 2.78; N, 14.51; I, 45.19%. Calcd for $C_5H_{16}N_6OSI_2Ru$: Ru, 18.1; C, 10.66; H, 2.86; N, 14.92; I, 45.07%. UV for **11** 23200 (sh, ε/mol^{-1} dm^{3} $^{-1}$ 104), 31900 (ε 936), and 39900 cm^{-1} (ε 2900).

***cis*-[Ru(NCS)(en)$_2$NO]I$_2$·H$_2$O (12):** An aqueous solution of **3** (1 mmol in 75 cm^3) containing NaNCS (5 mmol) was boiled for 10 min. For the resultant solution, the same column chromatography, removal of NaCl, and crystallization as that used for the preparation of **8** were applied. From the third band, **10** was obtained, which was identified by its UV and IR spectra: yield, 30%. From the fourth orange band, orange crystals (**12**) were obtained: yield 10% Found: Ru, 17.0; C, 10.14; H, 3.07; N, 14.08; H_2O, 2.6%. Calcd for $C_4H_{18}N_6O_2SI_2Ru$: Ru, 17.4; C, 10.33; H, 3.12; N, 14.66; H_2O, 3.1%. UV 20600 (ε/mol^{-1} dm^3 cm^{-1} 66.6), 27400 (ε 690), and 37100 cm^{-1} (ε 2100).

***trans*-[Ru(H$_2$O)(en)$_2$NO]Cl$_3$ (13):** The chloride of **1** was used as a starting material. **1** (2 mmol) dissolved in 10 cm^3 of water was passed through an anion exchange column (MCI GEL ϕ 1×10 cm, Cl$^-$ form). The eluate was collected and evaporated up on a rotary evaporator. The residue was dissolved in concd HCl (10 cm^3), and ethanol (30 cm^3) was carefully layered over the solution. The vessel was sealed, and left standing at room temperature. Several days after, yellowish-orange prismatic crystals were obtained. The crystals were collected by filtration, washed with concd HCl and ethanol successively, and air dried: yield, 88%. Found: Ru, 26.6; C, 12.92; H, 4.74; N, 18.43; Cl, 27.36%. Calcd for $C_4H_{18}N_5O_2Cl_3Ru$: Ru, 26.9; C, 12.79; H, 4.83; N, 18.64; Cl, 28.31%. UV 23500 (ε/mol^{-1} dm^3 cm^{-1} 17.8).

***cis*- [Ru(H$_2$O)(en)$_2$NO]I$_3$ (14):** An aqueous NaOH solution was added to an aqueous solution of *cis*-[RuCl$_2$(en)$_2$]Cl·H$_2$O (0.5 mmol in 30 cm^3) with stirring until the pH was greater than 11. The color of the solution changed from yellowish orange to dark green; *Immediately*, 70 vol% $HClO_4$ was added to the solution until the pH was less than 2. An aqueous solution of Ag_2O (0.75 mmol in 10 cm^3) containing a drop of the $HClO_4$ was added to the solution, and the produced AgCl was removed by filtration. NO gas was bubbled through the filtrate for 1 h. The same procedures for the column chromatography, removal of NaCl, and crystallization as those used for the preparation of **8** were applied. From the third orange band, an orange precipitate (**14**) was obtained: yield, 57% Found: Ru, 16.2; C, 8.44; H, 3.04; N, 12.14; I, 53.13%. Calcd for $C_4H_{18}N_5O_2I_3Ru$: Ru, 15.5; C, 7.39; H, 2.79; N, 10.78; I, 58.57%. UV 29500 (ε/mol^{-1} dm^3 cm^{-1} 154).

Results and Discussion

Identification of the Prepared Complexes. The elemental analyses agreed well with the chemical formulae proposed for the complexes, except for the *cis* isomer of the aqua-complex (**14**). However, as mentioned later, the presence of the *cis* isomer could be confirmed by the NMR and IR spectra.

^{13}C NMR Spectra: The ^{13}C NMR data are given in Table 1. For **1**, **2**, **4**, **6**, **8**, **11**, and **13**, only one resonance signal due to the methylene carbons of the en was observed, indicating that these complexes are of the *trans* form in which the four methylene carbons in the two ethylenediamine ligands are equivalent. On the other hand, for **3**, **5**, **7**, **9**, **12**, and **14**, four resonance signals due to the methylene carbons were observed, indicating that these complexes are of the *cis* form, in which the four carbons in the two ethylenediamine ligands are nonequivalent. For **8**, signals due to the methyl and carboxyl carbons of the acetato ligand were observed at δ=24.26 and 178.31, respectively; those for **9** were observed at δ=22.68 and 175.36, respectively. For **11** and **12**, the signals due to the thiocyanato ligand were observed at δ=139.87 and 141.21, respectively.

For assigning the signals due to the methylene carbons for the *cis* complexes, COSY and C–H COSY were measured for the *cis*-iodo complex (**7**), because overlapping of the resonance signals due to the methylene protons caused confusion concerning the assignment, except for the complex. The signals observed at δ=45.20 and 46.20 were assigned to the methylene carbons in one of the ethylenediamine rings, and those at δ=46.68 and 47.30 to another ring. The resonance signal observed at the lowest field hardly shifted (δ=47.44 for X=Cl (**3**), 47.36 for X=Br (**5**), 47.30 for X=I (**7**), 46.92 for X=OAc (**9**), and 47.67 for X=NCS (**12**)). Thus, the signal at δ=47.30 for the iodo complex (**7**) was assigned to the carbon bound directly to the nitrogen which is situated in a position trans to the NO, and the signal at δ=46.68 to another carbon in the same ethylenediamine ring. The signal at δ=45.20 was assigned to the carbon bound directly to the nitrogen in another ring trans to the I and the signal at δ=46.20 to another carbon in the same ethylenediamine ring, because the signal due to latter carbon is expected to be observed neighboring the signal at δ=46.68.

^{14}N NMR Spectra: The thiocyanate ion can coordinate to a metal through either the N or S atom. Generally, the IR spectrum is measured for distinguishing this, but is not useful.[9] The ν(CN) of **11** was observed in the region of the wave numbers of typical N- and S-bonding, and that of **12** was observed in the region of S-bonding. The ν(CS) and δ(NCS), which are useful for distinguishing the N- from S-bonding, were obscured by the bands due to the en. The NCS ligands in K$_2$[Ru(NCS)$_5$NO] was characterized as N-bonding using the ^{14}N NMR spectrum.[10] The resonance signal due to the nitrogen atom of the S-coordinate ligand was observed at a lower field than that of the free thiocyanate ion, while that of the N-coordinate ligand was observed at a higher field. For **11** and **12**, the resonance signals due to the NO were observed at −36 and −30 ppm, respectively, and due to the amine nitrogens of the en, were observed at −380 and −379 ppm, respectively. These signals were assigned in comparison with the resonance signals of K$_2$[RuCl$_5$NO] (−42 ppm) and of *trans*-[Ru(OH)(en)$_2$NO]I$_2$ (**1**) (−376 ppm). The

Table 1. IR and ^{13}C NMR Spectral Data of the Synthesized Complexes with Their Assignments

Complex	IR (Nujol) ν/cm^{-1} Selected bands	^{13}C NMR/δ DMSO-d_6/TMS
1	3840 ν(OH), 1865 ν(NO)	44.85 (CH_2)
2	1890 ν(NO), 330 ν(Ru–Cl)	45.51 (CH_2)
3	1910, 1890 ν(NO), 328 ν(Ru–Cl)	47.44, 45.64, 45.29, 44.39 (CH_2)
4	1880 ν(NO), 225 ν(Ru–Br)	45.81 (CH_2)
5	1901, 1880 ν(NO), 225 ν(Ru–Br)	47.36, 46.09, 45.61, 44.69 (CH_2)
6	1870 ν(NO), 175 ν(Ru–I)	46.55 (CH_2)
7	1900, 1880 ν(NO), 180 ν(Ru–I)	47.30, 46.68, 46.20, 45.20 (CH_2)
8	1890 ν(NO), 1630 ν(CO)	178.31 (COO^-), 45.21 (CH_2) 24.26 (CH_3)
9	1900 ν(NO), 1620, 1600 ν(CO)	175.36 (COO^-), 46.92, 44.86, 44.59, 44.03 (CH_2), 22.68 (CH_3)
10	2050, 2070 ν(CN), 1885 ν(NO)	
11	2055 ν(CN), 1880 ν(NO)	139.87 (NCS), 45.62 (CH_2)
12	2120 ν(CN), 1900 ν(NO)	141.21(NCS), 47.67, 45.76, 44.89, 44.47 (CH_2)
13	1900 ν(NO)	45.06 (CH_2)
14	3450br ν(OH), 1900, 1875 ν(NO)	47.90, 45.22, 45.10, 44.40 (CH_2)

resonance signals due to the NCS for **11** and **12** were assigned to those at −243.2 and −279.4 ppm, respectively. The resonance signal due to the NCS^- ion in an aqueous solution of KNCS was observed at −176.0 ppm. These observations indicate that the thiocyanato ligand is N-bonding. X-Ray diffraction analyses clearly show that both **11** and **12** contain an N-bonding thiocyanato ligand.[11]

^{1}H NMR Spectra: In all of the *trans* isomers, only one resonance signal due to the methylene carbons was observed. Interestingly, two resonance signals due to the amine protons and those due to the methylene protons were observed; the integrated intensity ratio of the four resonances was 1 : 1 : 1 : 1. The spectral data are listed in Table 2. For **8** and **9**, the resonance signal due to the methyl protons (3H) of the OAc ligand was observed over a reasonable range. The signals due to the methylene and the amine protons of **1** shifted to a higher field than those of the other complexes, except for **13** and **14**. Because the NO ligand of **1** shows the weakest NO^+ character in the series of complexes, as found from the ν(NO) (see IR data), the signals shifted to a higher field. On the other hand, the signals of **13** and **14** shifted to a lower field, which was caused by the more positive charge (3+) of the complexes.

The COSY and C–H COSY spectra for **1** were measured as an additional investigation. In the COSY spectra, correlations were found among all of the signals. On the other hand, in the C–H COSY spectra two resonance signals due to the methylene protons correlated with a signal due to the methylene carbon. These data suggest that the geminal methylene protons as well as the two geminal amine protons are in a different magnetic environment. The same phenomenon has been found in *fac*-$[RuCl_3(en)NO]$.[7] The conformation of the ethylenediamine ring in the complexes was found to be easily inverted at room temperature, as well as found in the mono(ethylenediamine) complexes.[7] Thus, the resonance signals are observed at their average positions. In the $\{Ru^{II}–NO^+\}$-type complexes, the multiplicity of the bond in the RuNO group exists not only in N–O, but also in Ru–NO. Figure 1 shows a schematic view of the protons at the average positions as well as the chemical shifts of these signals for $[RuX(en)_2NO]^{2+}$ (X=Cl, Br, I, OAc, and NCS). Generally, the magnetic anisotropy caused by the multiplicity of the bond induces a corn-shaped magnetic field; a deshielding effect inside of the corn and a shielding effect outside of the corn were observed for the double bond; the reverse effect was observed for the triple bond. The shielding effect due to the halogeno ligand also influences the neighboring nuclei. The double-bond character in Ru–N–O induces a shielding effect on the signals due to the methylene and the amine protons which are situated outside of the corn, and induces a deshielding effect on those which are situated inside of the corn. Thus, the signals due to the amine protons are assigned as follows. One of the signals due to the amine proton in the lower field is due to the proton (Ha) directed to X; another (Hb) is directed to NO, because based on X-ray diffraction, the former can be situated inside of the corn and the latter is situated outside of the corn.[11] For the resonance signals due to the methylene protons, the signal in lower field is due to a proton (Hc) directed to X; the other is a proton (Hd) directed to NO, because the latter is expected to be influenced by the shielding effect more than the former, though both the protons are situated in the shielding region. On the other hand, for these signals, the larger X causes a higher shift for the Ha signal, and gives a lower shift for the Hb, Hc, and Hd signals. For the X (X=Cl, Br, or I), which is situated in a position *trans* to the NO, the larger X causes a

Table 2. ^{1}H NMR Spectral Data of the Synthesized Complexes with Their Assignments

Complex	Methylene	Amine	Others
		trans Form	
1	2.67 (t, 2H), 2.91 (t, 2H)	4.90 (br, t, 2H), 5.74 (br, t, 2H)	4.36 (s, 1H, OH)
2	2.75 (t, 2H), 2.97 (t, 2H)	5.45 (br, t, 2H), 6.36 (br, t, 2H)	
4	2.80 (t, 2H), 3.04 (t, 2H)	5.55 (br, t, 2H), 6.28 (br, t, 2H)	
6	2.81 (t, 2H), 3.10 (t, 2H)	5.64 (br, t, 2H), 6.15 (br, t, 2H)	
8	2.78 (q, 2H), 2.86 (q, 2H)	5.64 (br, t, 2H), 6.16 (br, t, 2H)	1.93 (s, 3H, CH_3)
10	2.78 (m, 2H), 2.89 (m, 2H)	5.60 (br, t, 2H), 6.09 (br, t, 2H)	
13	2.81 (t, 2H), 3.02 (t, 2H)	5.79 (br, t, 2H), 6.62 (br, t, 2H)	
		cis Form	
3	2.73—3.10 (m, 8H)	5.43 (br, m, 1H), 5.57 (br, m, 1H), 5.75 (br, m, 1H), 5.85 (br, m, 1H), 6.13 (br, m, 2H), 6.19 (br, m, 1H), 6.46 (br, m, 1H)	
5	2.71—3.18 (m, 8H)	5.53 (br, m, 1H), 5.84 (br, m, 1H), 5.94 (br, m, 2H), 6.16 (br, m, 1H), 6.35 (br, m, 2H), 6.50 (br, m, 1H)	
7	2.66—3.21 (m, 8H)	5.44 (br, m, 3H), 5.89 (br, m, 1H), 6.10 (br, m, 1H), 6.21 (br, m, 1H), 6.37 (br, m, 2H)	
9	2.64—3.04 (m, 8H)	5.12 (br, m, 1H), 5.41 (br, m, 1H), 5.67 (br, m, 2H), 5.74 (br, m, 1H), 5.85 (br, m, 1H), 6.03 (br, m, 1H), 6.27 (br, m, 1H)	2.01 (s, 3H, CH_3)
12	2.67—3.17 (m, 8H)	6.00 (br, m, 1H), 6.30 (br, m, 1H), 6.45 (br, m, 2H), 6.61 (br, m, 1H), 6.68 (br, m, 1H), 6.80 (br, m, 1H), 6.91 (br, m, 1H)	
14	2.68—3.10 (m, 8H)	5.74 (br, m, 1H), 6.16 (br, m, 1H), 6.27 (br, m, 1H), 6.78 (br, m, 3H), 7.06 (br, m, 1H), 7.13 (br, m, 1H)	

weaker N–O bond, thus leading to a degeneracy of the magnetic anisotropy to the protons. An enlargement of X causes a stronger Ru–N (NO) bond; a subsequent increase in the multiplicity of the bond leads a degeneracy of the magnetic anisotropy accompanying a reversal of the magnetic-anisotropy effect. Therefore, an enlargement of X causes a degeneration of the magnetic anisotropy due to the Ru–N–O bonds to the protons. Thus, the larger X causes a lower shift for Hb, Hc, and Hd, and the higher shift for Ha is enhanced by a shielding effect caused by the neighboring X. The shielding effect is more enhanced by X=NCS and OAc because of the double-bond(s) character in themselves. For the resonance signals of **1** and **13**, the same assignment is performed.

In a series of *cis* isomers, resonance signals due to the methylene protons were observed in the region $\delta=$ 2.64—3.21 with overlapping; however, those due to the amine protons were rather split, indicating that the signals are influenced by the magnetic anisotropy, as observed in the case of the *trans* isomers. However, the signals were complicated by electronic interactions caused by the unsymmetrical feature of the isomers. An overlapping of the signals due to the methylene protons causes some difficulty in assigning of the signals. Therefore, a further examination of the magnetic anisotropy observed in the *cis* isomers could not be performed.

IR Spectra: The IR data are summarized in Table 1. In all of the complexes, ν(NO) was observed in the region 1865—1900 cm^{-1}, indicating that the synthesized complexes are of the $\{Ru^{II}–NO^+\}$-type.[1—3] Although the ν(CO) due to the acetato ligand of **8** and **9** was observed in the 1600—1630 cm^{-1} region, another ν(CO), which is expected to be observable at around 1400 cm^{-1}, was obscured by the bands due to the en. In a series of *trans*-$[RuX(en)_2NO]^{2+}$ isomers, the ν(NO) decreased in the order Cl≈OAc>Br≈NCS>I>OH. These reflect the degree of π-donor ability of ligand X *trans* to the NO; the larger π-donor ability of X causes a smaller ν(NO), because the NO withdraws the π-electron density from the X through Ru. On the other hand, in a series of the *cis* isomers, the ν(NO) showed no significant variation with X. The same phenomena have been observed in a series of *mer*-$[RuX_3(en)NO]$ (X=Cl, Br, and I).[7] This indicates that a π-donation of the aniono ligand *cis* to the NO does not influence ν(NO). Thus, the degree of π-donor ability of the ligands increase in the order Cl≈OAc<Br≈NCS<I<OH. The ν(NO) of **13** (the *trans* isomer) was the same as that of **14** (the *cis* isomer), suggesting that the σ-donor ability

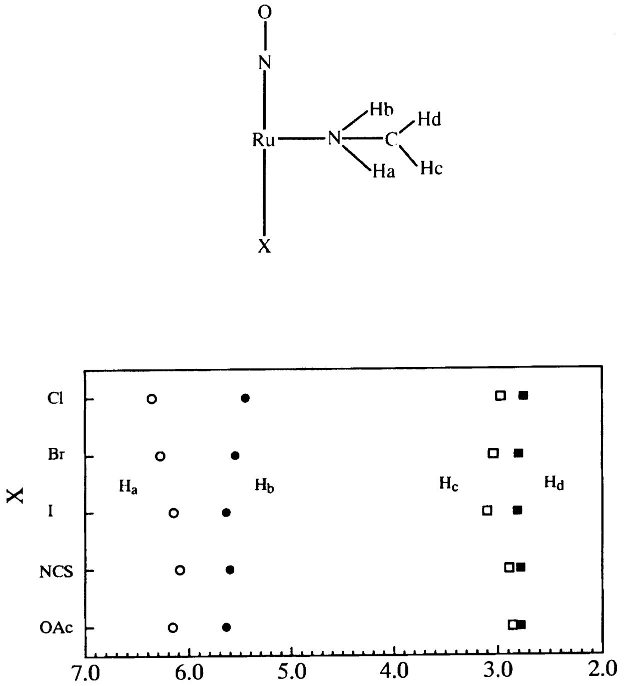

Fig. 1. Schematic view of the protons at an avarage position and the chemical shifts of the ^{1}H NMR signals for *trans*-$[RuX(en)_2NO]^{2+}$ (X=Cl, Br, I, OAc, and NCS).

of H_2O is comparable to that of en.

In **3**, **5**, or **7** (the *cis* isomer), although the ν(NO) band in Nujol mull split into two bands, no splitting was observed in a DMSO solution; **3**, 1895 cm^{-1}; **5**, 1895 cm^{-1}; **7**, 1890 cm^{-1}. The same phenomenon has been observed in $[Ru(NH_3)_5NO]Cl\cdot H_2O$[12] and a series of *mer*-$[RuX_3(en)NO]$ (X=Cl, Br, and I).[7] In the former, the splitting has been explained as being due to an interaction between the NO and the counter anion; however, this explanation can not be applied to the latter case. It has been reported that in *trans*-$[Rh(CN)_2(tn)_2]ClO_4$ (th=trimethylenediamine), a slight difference in the conformation of the tn ligands in the crystal lattice affects ν(CN).[13] A slight difference in the conformation of the en may cause a splitting of ν(NO) in the polycrystals which are used for IR measurements using the Nujol mull method.

UV-vis Spectra: The UV-vis spectra of the prepared complexes were characteristic of the *trans* and *cis* isomers, whose spectra are comparable to those of the corresponding tetraammine complexes.[14—16] This supports that identification of the prepared complexes as being reasonable.

Isomerization of the Complexes. *trans*-$[RuX(en)_2NO]^{2+}$ (X=Cl, Br, I, or OAc) was prepared from *trans*-$[Ru(OH)(en)_2NO]^{2+}$ by a substitution reaction from OH^- of the X^-; *cis*-$[RuX(en)_2NO]^{2+}$ (X=Cl, Br, I) was also prepared by an isomerization reaction accompanied by a substitution reaction from OH^- to the X^-. *cis*-$[Ru(NCS)(en)_2NO]^{2+}$ was prepared by treating *cis*-$[RuCl(en)_2NO]^{2+}$ with the thiocyanate ion while boiling for 10 min. For even longer boiling (2 h), the *trans* isomer was prepared.

For the chloro or bromo complex, *trans*-to-*cis* isomerization was not observed upon refluxing the *trans* isomer in an aqueous media (1 mol dm^{-3} HCl or HBr, and 1 mol dm^{-3} NaCl or NaBr); *cis*-to-*trans* isomerization was also not observed under the same experimental conditions. These facts suggest that isomerization in the preparation occurs along with a ligand-substitution reaction. On the other hand, the *trans*-iodo complex isomerized to the *cis* complex by refluxing in 1 mol dm^{-3} HI, and *cis*-thiocyanato complex isomerized to the *trans* complex by refluxing in 1 mol dm^{-3} NaNCS. These isomerization reactions were not observed in the absence of either the iodide ion or the thiocyanate ion.

Thus, two kinds of isomerization reactions were found to be involved in the preparation of the bis(ethylenediamine)-type complexes: One was accompanied by a substitution reaction from OH^- to X^-; the other occurred after a substitution reaction. For the chloro and bromo complexes the former is predominant, and for the iodo and thiocyanato complexes the latter is predominant. Nucleophilic interaction of these ions (for *trans*-iodo complex, it is probably I_3^-) with NO^+ promotes isomerization, because I^- and NCS^- can behave as nucleophilic reagents and Cl^- and Br^- are weaker nucleophiles than I^- and NCS^-. In the substitution reaction from OH^- to X^- (X=Cl and Br), *trans*-$[Ru(H_2O)(en)_2NO]^{3+}$ is an intermediate, and the isomerization reaction accompanied by the substitution reaction occurs through this complex. Because the NO group of the aqua-complex is expected to show strongest electrophilic behavior in the series, the complex can suffer a nucleophilic attack of the X^- ions.

For all of the complexes, ligand X was substituted immediately by OH^- when sodium hydroxide was added; thus, for the *cis* complexes the isomerization was accompanied. The intermediate in the isomerization from *cis*- to *trans*-$[Ru(OH)(en)_2NO]^{2+}$ could not be detected because of the speed of the reaction. The nucleophilic interaction of OH^- with NO^+ can be related with these substitution reactions accompanied by isomerization. For the *trans*-aqua complex, the aqua ligand was labile in the solution. The complex was immediately converted to the *trans*-hydroxo complex in H_2O. Although the aqua ligand was partially dissociated, even in 1 mol dm^{-3} HCl (the abundance of the *trans*-hydroxo complex was 13%), dissociation was not found in 6 mol dm^{-3} and concd HCl.

The authors are sincerely grateful to Mr. Shingo Kouda, Ms. Risa Asanuma, Ms. Akiko Miyakawa, and Ms. Chisako Sakamoto for their technical assistance concerning synthesis of the complexes.

References

1) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).

2) K. G. Caulton, *Coord. Chem. Rev.*, **14**, 317 (1975).

3) F. Bottomley, *Coord. Chem. Rev.*, **26**, 7 (1978).

4) E. A. Seddon and K. R. Seddon, "The Chemistry of Ruthenium," Elsevier, Amsterdam (1984), pp. 1130—1138.

5) A. Werner and A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 737 (1920).

6) R. Charronat, *Ann. Chim.*, **16**, 227 (1931).

7) H. Tomizawa, K. Harada, E. Miki, K. Mizumachi, T. Ishimori, A. Urushiyama, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **66**, 1658 (1993).

8) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc. A*, **1967**, 546.

9) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed, John Wiley and Sons, New York (1986), pp. 282—287

10) O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, **1964**, 3335.

11) H. Tomizawa, E. Miki, K. Mizumachi, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, **67**, 1816 (1994).

12) F. Bottomley, *J. Chem. Soc., Dalton Trans.*, **1974**, 1600.

13) N. Odano, K. Harada, and A. Urushiyama, *Bull. Chem. Soc. Jpn.*, **66**, 1991 (1993).

14) A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, **11**, 880 (1972).

15) S. Pell and J. N. Armor, *Inorg. Chem.*, **12**, 873 (1973).

16) N. M. Sinitsyn, V. V. Borisov, and L. A. Pshenichnilova, *Russ. J. Inorg. Chem.*, (*Engl. Transl.*), **19**, 1667 (1974).