Crystal Structures 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
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The structures of *trans*-[RuX(en)$_2$NO]X$'_2$ (X=OH (**1**), Cl (**3**), or NCS (**4**), en=ethylenediamine, X$'$=Br (**1**), Cl (**3**), or NCS (**4**)), *trans*-[Ru(H_2O)(en)$_2$NO]Cl_3 (**2**), *cis*-[RuX(en)$_2$NO]XPF_6 (X=Cl (**5**), or Br (**6**)), and *cis*-[Ru(NCS)(en)$_2$NO]$I_2\cdot H_2O$ (**7**) were determined by X-ray diffraction. In two pairs of the geometrical isomers (**3** and **5**, and **4** and **7**), the Ru–Cl or the Ru–N(NCS) bond for the *trans* isomer was shorter than that for the *cis* isomer due to a *trans*-strengthening effect of the NO; this effect was not observed for the corresponding Ru–N(en) bond. These facts indicate that the effect is mainly caused by both σ- and π-bonding interactions of the ligand *trans* to NO through Ru, and is not caused by only the σ-donation of the ligand.

Both weak σ-donor and strong π-acceptor abilities inhere in coordinated NO^+, which causes a *trans*-strengthening effect.[1] This effect has been investigated concerning the {Ru^{II}–NO^+}-type of mononitrosyl complexes.[1—3] The {Ru^{II}–NO^+}-type complexes containing ammine ligands, which show a σ-bonding ability, have also been extensively studied.[4] However, complexes containing ethylenediamine ligands, which show only a σ-bonding ability are not known, except for two classical examples.[5,6] Recently, we have reported on the structures of *mer*-[RuX_3(en)NO] (X=Cl, Br, or I),[7] *trans-mer*-[$RuCl_2$(dien)NO]PF_6,[8] and *mer*-[$RuBr_3$(Hdien)NO]Br[8] in which en, dien, and Hdien show only a σ-bonding ability on coordination. The *trans*-strengthening effect has not been found in these Ru–N(en, dien, or Hdien) bonds. For a further examination of the *trans*-strengthening effect caused by NO, the structures of a series of anionobis(ethylenediamine)-nitrosylruthenium(II) complexes containing two pairs of *trans* and *cis* isomers have newly been determined by X-ray diffraction.

Experimental

Materials. The syntheses of *trans*-[Ru(OH)(en)$_2$NO]-I_2, *trans*-[Ru(H_2O)(en)$_2$NO]Cl_3 (**2**), *trans*-[RuCl(en)$_2$NO]-Cl_2 (**3**), *trans*-[Ru(NCS)(en)$_2$NO](NCS)$_2$ (**4**), *cis*-[RuCl-(en)$_2$NO]Cl_2, *cis*-[RuBr(en)$_2$NO]Br_2, and *cis*-[Ru(NCS)-(en)$_2$NO]$I_2\cdot H_2O$ (**7**) were carried out by recently reported methods.[9] *trans*-[Ru(OH)(en)$_2$NO]Br_2 (**1**) was prepared as follows: The counter-anion (I^-) of *trans*-[Ru(OH)(en)$_2$NO]-I_2 was changed to Cl^- using an anion exchange column (MCI GEL, Cl^- form, ϕ, 1×6 cm); to the eluate an excess of NaBr was added in order to precipitate **1**. *cis*-[RuCl-(en)$_2$NO]Cl(PF_6) (**5**) and *cis*-[RuBr(en)$_2$NO]Br(PF_6) (**6**) were prepared by treating the corresponding chloride and bromide with $NaPF_6$, respectively.

Preparation of Single Crystals for an X-Ray Crystal Analysis. To **1** (500 mg) dissolved in water (10 cm^3) ethanol was added until faint turbidity appeared; moreover, ethanol vapor was diffused into the solution at room temperature. Several days later, yellow needle crystals were obtained. Yellow plate crystals of **2** were chosen from crystals obtained in the process of synthesizing of the complex. To obtain yellowish-orange plate crystals of **3**, the same procedure as that used for preparation of the crystals of **1** was carried out. **4** (200 mg) dissolved in water (30 cm^3) was allowed to evaporate at room temperature. Several days later, yellowish-orange prismatic crystals were obtained. The same procedure as that used for preparation of the crystals of **4** was carried out for **5** (orange prismatic), **6** (reddish orange prismatic), and **7** (brown plate).

X-Ray Crystal Analysis. A similar data-collection method was applied for each of the crystals. The crystal data and measurement conditions for the intensity collection of the *trans* and *cis* complexes are given in Tables 1 and 2, respectively. The crystals were mounted on a Rigaku AFC-5 automated fourcircle diffractometer, and intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å, 50 kV and 37.5 mA) at room temperature. The lattice parameters were obtained by a least-squares refinement using 20 reflections ($20°\leq 2\theta \leq 25°$). For weak reflections, the measurements were repeated up to four times. The crystal stability was monitored by recording three standard reflections every 100 reflections; no significant variations were observed, except for the **2**. Because the intensities of the standard reflections for **2** decreased with the irradiation time (the minimum $F/F_{initial}$ was 66.7%), weaker radiation (40 kV and 32.5 mA) was carried out for the intensity data collection of the crystal; the minimum $F/F_{initial}$ was the 93.8%. For an absolute configuration determination of **3** and **7**, a pair of *hkl* and $\bar{h}\,\bar{k}\,\bar{l}$ was measured. For a structure determination and refinement, the intensity data of unique reflections with $|F|\geq 3\sigma(|F|)$ from the collected reflections were used. The intensities were corrected for any Lorentz and polarization effects. An absorption correction was also applied using a published method of North et al.[10] All of the calculations were carried out on a FACOM M-760 computer using the UNICS III Program System[11] at the Computer Center of Rikkyo University. The structures were solved by the heavy-atom method and finally refined by a full-matrix least-squares method, except for **1**, **5**, and **6**, whose structures were refined by a block-diagonal least-squares method. For **1**, **2**, **3**, **4**, **5**, or **7**, the hydrogen atoms which were observed in difference Fourier syntheses were included in the refinement. The other hydrogens, except for the OH group of **1** and H_2O of **2** and **7**, were placed at the calculated positions, and were not included in the refinement. The final R values were 0.056 for **1**, 0.036 for **2**, 0.020 for **3**, 0.044 for **4**, 0.053 for **5**, and 0.035 for **7** with anisotropic temperature factors for all of the atom, except

Table 1. Crystal Data and Experimental Conditions for Intensity Collection of the *trans* Complexes

Parameter	$[Ru(OH)(en)_2NO]Br_2$ (**1**)	$[Ru(H_2O)(en)_2NO]Cl_3$ (**2**)	$[RuCl(en)_2NO]Cl_2$ (**3**)	$[Ru(NCS)(en)_2NO](NCS)_2$ (**4**)
Formula	$RuBr_2O_2N_5C_4H_{17}$	$RuCl_3O_2N_5C_4H_{18}$	$RuCl_3ON_5C_4H_{16}$	$RuS_3ON_8C_7H_{16}$
MW	428.09	375.65	357.63	425.51
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Cmc2_1$	$Pna2_1$	$P2_12_12_1$	$Pmn2_1$
a/Å	17.511(7)	15.507(6)	10.016(2)	13.821(8)
b/Å	8.037(6)	8.447(1)	12.114(2)	6.939(1)
c/Å	9.078(9)	10.089(3)	9.939(48)	8.6305(9)
V/Å^3	1277.5(18)	1321.5(7)	1205.9(59)	827.6(5)
Z	4	4	4	2
D_m/g cm^{-3}	2.21	1.90	1.98	1.70
D_c/g cm^{-3}	2.23	1.89	1.97	1.71
Crystal size/mm	0.2×0.3×0.4	0.2×0.3×0.3	0.2×0.2×0.2	0.1×0.2×0.2
μ(Mo $K\alpha$)/cm^{-1}	73.92	17.69	19.28	13.00
F(000)	412	752	720	428
Scan mode	$\omega(2\theta\leq25°)$ ω–$2\theta(25°\leq2\theta\leq55°)$	$\omega(2\theta\leq25°)$ ω–$2\theta(25°\leq2\theta\leq55°)$	$\omega(2\theta\leq25°)$ ω–$2\theta(25°\leq2\theta\leq55°)$	$\omega(2\theta\leq25°)$ ω–$2\theta(25°\leq2\theta\leq55°)$
Scan width	1.10+0.45 tan θ	1.10+0.45 tan θ	1.10+0.45 tan θ	1.10+0.45 tan θ
No. of reflections collected	696	1238	2459	962
No. of reflections with $\|F\|\geq3\sigma(\|F\|)$	644	1229	2143	914
R[a]	0.056	0.036	0.020	0.044
R_w[b]	0.064	0.050	0.020	0.045

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

Table 2. Crystal Data and Experimental Conditions for Intensity Collection of the *cis* Complexes

Parameter	$[RuCl(en)_2NO]ClPF_5$ (**5**)	$[RuBr(en)_2NO]BrPF_6$ (**6**)	$[Ru(NCS)(en)_2NO]I_2\cdot H_2O$ (**7**)
Formula	$RuCl_2PF_6ON_5C_4H_{16}$	$RuBr_2PF_2ON_5C_4H_{16}$	$I_2RuSO_2N_6C_5H_{18}$
MW	467.14	556.05	581.18
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/a$	$P2_1/a$	$P2_12_12_1$
a/Å	12.407(4)	12.901(6)	20.299(10)
b/Å	13.458(2)	13.954(2)	10.238(7)
c/Å	9.591(2)	9.312(7)	8.054(2)
β/°	107.5(8)	108.39(5)	
V/Å^3	1527.5(8)	1590.8(1.5)	1673.8(15)
Z	4	4	4
D_m/g cm^{-3}	2.03	2.32	2.31
D_c/g cm^{-3}	2.03	2.31	2.31
Crystal size/mm	0.3×0.4×0.4	0.1×0.1×0.2	0.2×0.2×0.3
μ(Mo $K\alpha$)/cm^{-1}	15.27	61.04	46.93
F(000)	920	1064	1088
Scan mode	$\omega(2\theta\leq25°)$ ω–$2\theta(25°\leq2\theta\leq55°)$	$\omega(2\theta\leq25°)$ ω–$2\theta(25°\leq2\theta\leq55°)$	$\omega(2\theta\leq25°)$ ω–$2\theta(25°\leq2\theta\leq55°)$
Scan width	1.10+0.45 tan θ	1.10+0.50 tan θ	1.10+0.45 tan θ
No. of reflections collected	3719	2865	3324
No. of reflections with $\|F\|\geq3\sigma(\|F\|)$	2879	2147	2742
R[a]	0.053	0.098	0.035
R_w[b]	0.052	0.111	0.037

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

for the hydrogen atoms, and with isotropic factors for the hydrogen atoms. For **6**, although several electron-density peaks, which could be assigned to the hydrogen atom, were observed in difference Fourier syntheses, these were not included in the refinement; the final R value was 0.098 with anisotropic temperature factors. The atomic scattering factors were taken from the standard sources[12] for the non-hydrogen atoms and from the published data of Stewart et al.[13] for the hydrogen atoms. The positional and thermal parameters are given in Table 3.

For **1**, **2**, **3**, **4**, and **7**, the solution and refinement provide good R values and reasonable temperature factors. For **5**, their atoms, especially the F and C3 atoms, have larger temperature factors. Thus, although a reexamination of the atomic position on a Fourier map or difference Fourier map was attempted; a more suitable atomic position or disorder

Table 3. Positional and Thermal Parameters with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}[a)]/Å^2
	trans-[Ru(OH)(en)$_2$NO]Br$_2$ (**1**)			
Ru	0	0.2061(2)	0.2500(4)	1.6
Br	0.1257(1)	0.6996(3)	0.2564(4)	2.4
O1	0	0.467(3)	0.481(4)	4.9
O2	0	0.013(3)	0.121(2)	2.3
N1	0	0.369(2)	0.385(3)	2.3
N2	0.094(1)	0.302(2)	0.131(2)	2.8
N3	0.090(1)	0.089(2)	0.374(2)	2.7
C1	0.163(1)	0.206(4)	0.162(2)	3.6
C2	0.166(1)	0.183(4)	0.333(3)	3.9
	trans-[Ru(H$_2$O)(en)$_2$NO]Cl$_3$ (**2**)			
Ru	0.10787(5)	0.2178(1)	0.2500(2)	1.1
Cl1	0.2309(2)	0.6128(4)	0.1522(4)	2.5
Cl2	−0.1393(2)	0.4418(5)	0.2953(4)	2.7
Cl3	0.0341(3)	−0.1865(4)	0.3811(4)	2.8
O1	−0.0623(6)	0.093(1)	0.198(1)	3.4
O2	0.2302(5)	0.307(1)	0.2895(9)	2.1
N1	0.0057(7)	0.144(1)	0.220(1)	1.8
N2	0.1306(7)	0.289(1)	0.049(1)	1.8
N3	0.1670(7)	0.008(1)	0.181(1)	1.8
N4	0.0658(7)	0.438(1)	0.329(1)	1.6
N5	0.1055(8)	0.153(1)	0.452(1)	1.8
C1	0.194(1)	0.176(2)	−0.008(1)	2.5
C2	0.169(1)	0.010(2)	0.035(1)	2.2
C3	0.075(1)	0.434(2)	0.477(1)	2.0
C4	0.051(1)	0.272(2)	0.526(1)	2.3
	trans-[RuCl(en)$_2$NO]Cl$_2$ (**3**)			
Ru	0.24060(2)	0.24582(2)	0.25161(2)	1.5
Cl1	0.2054(1)	0.16381(8)	0.04127(9)	2.5
Cl2	0.3517(1)	0.42958(8)	−0.0938(1)	2.9
Cl3	0.6105(1)	0.39558(8)	0.4146(1)	3.0
O	0.2829(3)	0.3398(2)	0.5139(3)	3.3
N1	0.2672(3)	0.3060(2)	0.4126(3)	2.0
N2	0.1586(3)	0.3906(3)	0.1693(3)	2.0
N3	0.0389(3)	0.2151(3)	0.2940(3)	2.3
N4	0.4405(3)	0.2700(3)	0.1910(3)	2.1
N5	0.3198(3)	0.0937(3)	0.3169(4)	2.3
C1	0.0117(4)	0.3784(4)	0.1586(4)	2.5
C2	−0.0379(4)	0.3191(4)	0.2822(4)	2.6
C3	0.5158(4)	0.1642(4)	0.2054(4)	2.5
C4	0.4675(4)	0.1061(4)	0.3299(4)	2.6
	trans-[Ru(NCS)(en)$_2$NO](NCS)$_2$ (**4**)			
Ru	0	0.2431(1)	0.5000(3)	2.3
S1	0	−0.2470(7)	0.8558(6)	5.6
S2	0.3804	−0.2462(2)	0.5112(9)	5.8
O	0	0.583(2)	0.288(2)	5.9
N1	0	0.459(2)	0.374(2)	3.5
N2	0.1139(8)	0.375(1)	0.636(1)	3.1
N3	0.1162(7)	0.135(1)	0.383(1)	3.2
N4	0	0.038(1)	0.645(2)	3.0
N5	0.1793(6)	−0.242(1)	0.502(3)	5.5
C1	0.204(1)	0.266(2)	0.600(2)	3.2
C2	0.208(2)	0.228(3)	0.428(2)	4.4
C3	0	−0.092(3)	0.727(2)	2.8
C4	0.2622(6)	−0.238(1)	0.503(2)	3.6
	cis-[RuCl(en)$_2$NO]ClPF$_6$ (**5**)			
Ru	0.28277(4)	0.06746(4)	0.43357(6)	3.8
Cl1	0.3729(1)	−0.0857(1)	0.5163(2)	4.5
Cl2	0.5460(2)	−0.3503(1)	0.4801(3)	5.8
P	0.2786(2)	−0.1426(2)	0.0031(3)	5.6
F1	0.1748(7)	−0.1709(6)	0.0546(10)	13.2
F2	0.3762(7)	−0.1142(7)	−0.0516(10)	14.7
F3	0.3290(9)	−0.2446(6)	0.0320(10)	15.9
F4	0.2228(8)	−0.0387(9)	−0.0168(10)	13.7
F5	0.2140(7)	−0.1661(9)	−0.1550(8)	16.6
F6	0.3372(7)	−0.1151(8)	0.1602(9)	16.8
O	0.4003(5)	0.1131(5)	0.2236(7)	6.9
N1	0.3552(5)	0.0923(4)	0.3056(6)	4.4
N2	0.2028(5)	0.0506(4)	0.5966(7)	4.7
N3	0.4039(5)	0.1371(4)	0.6088(7)	4.8
N4	0.1488(5)	−0.0057(5)	0.2848(7)	4.8
N5	0.1772(6)	0.1906(5)	0.3606(9)	6.6
C1	0.2557(8)	0.1167(8)	0.7220(10)	7.1
C2	0.3774(8)	0.1226(9)	0.7500(11)	8.7
C3	0.0570(10)	0.0609(10)	0.2153(14)	11.2
C4	0.0888(8)	0.1659(7)	0.2328(12)	7.8

could not be found. The larger anisotropy on the temperature factor of the C3 atom suggests that a conformational inversion occurs partly on that ethylenediamine ligand. For **6**, the convergence is quite poor, and the hydrogen atoms were not included in a further refinement. However, the obtained result for **6** shows that this complex is isomorphous to **5**.

Because the space group of **3** and **7** is $P2_12_12_1$, and $Z=4$, respectively, the complexes were spontaneously resolved. These absolute configurations were determined by an anomalous-scattering technique and a convenient R-factor ratio test. The structure of the enantiomer of **3** was refined by using the same method as that for **3**. The refinements converged to $R=0.0272$ and $R_w=0.0329$ for the enantiomer and $R=0.0269$ and $R_w=0.0327$ for **3**. For **7** and the enantiomer, the same type of comparison was performed using a block-diagonal least-squares method with isotropic temperature factors; $R=0.079$ for **7** and $R=0.087$ for the enantiomer were obtained. Both results indicate that the structures of the enantiomers were rejected, though the difference in the former case is quite the small.

Tables of the anisotropic thermal parameters, coordinates of the hydrogen atoms and the complete F_o-F_c data are deposited as Document No. 67036 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Structures of the *trans* Complexes. ORTEP drawings of the complex cations of **1**, **2**, **3**, and **4** are

Table 3. (Continued)

Atom	x	y	z	B_{eq}[a)]/Å^2	Atom	x	y	z	B_{eq}[a)]/Å^2
	cis-[RuBr(en)$_2$NO]BrPF$_6$ (**6**)					*cis*-[Ru(NCS)(en)$_2$NO]I$_2$·H$_2$O (**7**)			
Ru	0.2841(1)	0.0735(1)	0.4336(2)	3.9	I1	−0.34774(8)	0.10768(4)	0.7181(1)	4.9
Br1	0.3727(2)	−0.0851(2)	0.5101(3)	4.0	I2	0.24564(8)	0.06996(3)	0.90208(8)	3.6
Br2	0.5443(2)	−0.3542(2)	0.4585(4)	5.8	Ru	0.03052(7)	0.11560(3)	0.42484(9)	2.3
P	0.2694(6)	−0.1399(5)	−0.0073(9)	5.6	S	0.07533(7)	0.26485(3)	0.8805(4)	4.6
F1	0.194(2)	−0.162(2)	0.088(3)	13.7	O1	−0.0394(4)	0.0103(4)	0.647(1)	5.3
F2	0.341(2)	−0.224(2)	0.058(4)	17.9	O2	−0.1155(9)	0.2842(4)	0.270(1)	5.0
F3	0.207(2)	−0.203(3)	−0.130(4)	20.1	N1	−0.0155(9)	0.0528(4)	0.562(1)	3.2
F4	0.340(2)	−0.116(2)	−0.106(3)	12.8	N2	0.1087(8)	0.1863(4)	0.261(1)	2.9
F5	0.196(2)	−0.053(2)	−0.066(5)	18.8	N3	0.2318(8)	0.1014(4)	0.2824(9)	2.8
F6	0.334(2)	−0.076(3)	0.117(4)	18.3	N4	−0.1600(8)	0.1416(4)	0.352(1)	3.1
O	0.396(1)	0.112(1)	0.222(2)	7.0	N5	0.0133(8)	0.0530(4)	0.219(1)	3.0
N1	0.352(2)	0.096(1)	0.305(2)	4.9	N6	0.0378(9)	0.1877(4)	0.602(1)	3.4
N2	0.208(1)	0.055(1)	0.602(2)	4.6	C1	0.243(1)	0.2025(5)	0.308(2)	3.7
N3	0.405(2)	0.134(1)	0.628(3)	5.1	C2	0.315(1)	0.1412(6)	0.349(1)	3.7
N4	0.148(2)	0.009(2)	0.266(2)	5.3	C3	−0.209(1)	0.0921(6)	0.228(2)	4.0
N5	0.186(2)	0.200(2)	0.358(3)	7.0	C4	−0.101(1)	0.0746(6)	0.114(1)	3.9
C1	0.258(2)	0.116(2)	0.736(3)	6.4	C5	0.054(1)	0.2186(5)	0.718(1)	3.0
C2	0.378(2)	0.118(2)	0.764(3)	6.6					
C3	0.078(3)	0.087(3)	0.176(6)	13.6					
C4	0.087(2)	0.175(2)	0.236(4)	6.9					

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

shown in Figs. 1, 2, 3, and 4, respectively, and their selected bond lengths and angles are listed in Table 4. In these complex cations, the two ethylenediamine rings are situated in a position *trans* to each other, and the ligand X (X=OH, H_2O, Cl, or NCS) is also situated in a position *trans* to the NO. This supports our previous characterization for the complexes based on the IR, UV-vis, and NMR spectra.[9] The space groups of **1** and **4** are $Cmc2_1$ and $Pmn2_1$, which have mirror symmetry, respectively. Because the mirror is along the X–Ru–NO axis, which includes the atoms, and is between the two ethylenediamine rings, the two ethylenediamine rings are equivalent, but are in the mirror image, so that the rings are in the $\delta\lambda$ gauche conformation. On the other hand, the two ethylenediamine rings of **2** and **3** are nonequivalent, because all of the atoms in the lattice

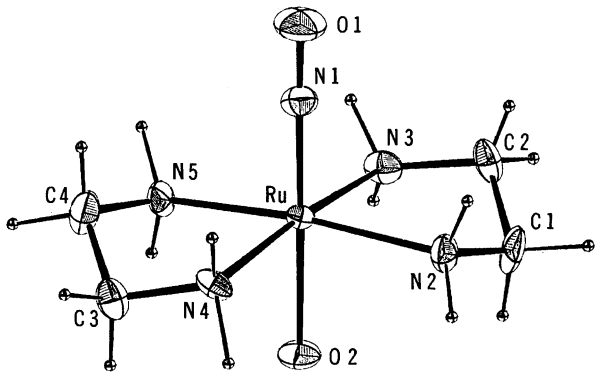

Fig. 2. ORTEP drawing and atomic numbering scheme of *trans*-[Ru(H$_2$O)(en)$_2$NO]$^{3+}$ (**2**).

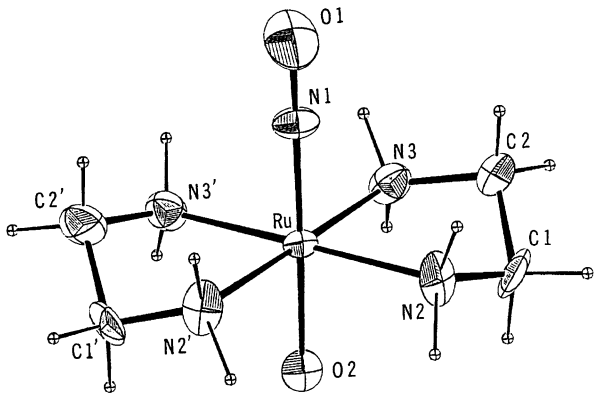

Fig. 1. ORTEP drawing and atomic numbering scheme of *trans*-[Ru(OH)(en)$_2$NO]$^{2+}$ (**1**).

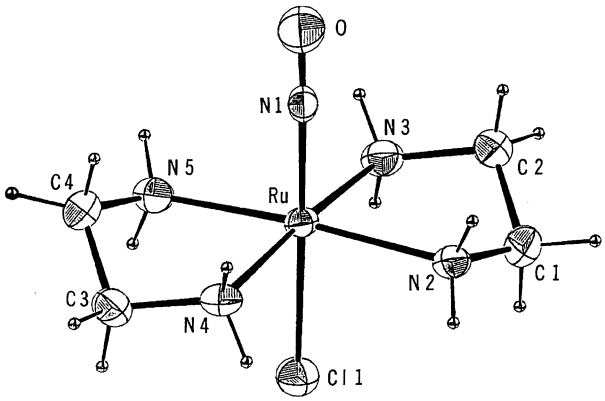

Fig. 3. ORTEP drawing and atomic numbering scheme of *trans*-[RuCl(en)$_2$NO]$^{2+}$ (**3**).

Table 4. Selected Bond Lengths (Å) and Angles (°) with Their Estimated Deviations in Parentheses of The *trans* Complexes

		trans-[Ru(OH)(en)$_2$NO]Br$_2$ (**1**)			
Ru–O2	1.94(2)	Ru–N3	2.16(2)	N3–C2	1.57(3)
Ru–N1	1.79(2)	O1–N1	1.18(4)	C1–C2	1.57(3)
Ru–N2	2.12(2)	N2–C1	1.46(3)		
N1–Ru–O2	174.0(10)	N3–Ru–O2	88.1(6)	Ru–N2–C1	110.8(14)
N1–Ru–N2	94.7(7)	N2–Ru–N2′	102.5(7)	N2–C1–C2	105.9(18)
N1–Ru–N3	87.9(7)	N2–Ru–N3′	174.9(7)	C1–C2–N3	105.8(17)
N2–Ru–O2	89.1(6)	N3–Ru–N3′	94.0(7)	C2–N3–Ru	106.4(13)
N2–Ru–N3	81.7(7)	Ru–N1–O1	174.8(24)		
		Hydrogen bonds[a)]			
N2–Br(A)	3.44(2)	N2–Br(B)	3.45(2)		
		trans-[Ru(H$_2$O)(en)$_2$NO]Cl$_3$ (**2**)			
Ru–O2	2.079(8)	Ru–N5	2.11(1)	N5–C4	1.51(2)
Ru–N1	1.73(1)	O1–N1	1.16(1)	C1–C2	1.51(2)
Ru–N2	2.14(1)	N2–C1	1.49(2)	C3–C4	1.50(2)
Ru–N3	2.11(1)	N3–C2	1.47(2)		
Ru–N4	2.13(1)	N4–C3	1.50(2)		
N1–Ru–O2	179.1(4)	N2–Ru–N5	171.4(5)	Ru–N2–C1	107.3(8)
N1–Ru–N2	94.8(5)	N3–Ru–O2	88.3(4)	N2–C1–C2	107.9(12)
N1–Ru–N3	92.1(5)	N3–Ru–N4	172.0(4)	C1–C2–N3	108.2(12)
N1–Ru–N4	95.8(5)	N3–Ru–N5	96.2(5)	C2–N3–Ru	109.0(9)
N1–Ru–N5	93.6(5)	N4–Ru–O2	83.8(4)	Ru–N4–C3	108.8(8)
N2–Ru–O2	86.0(4)	N4–Ru–N5	81.9(4)	N4–C3–C4	108.7(11)
N2–Ru–N3	81.6(5)	N5–Ru–O2	85.7(4)	C3–C4–N5	107.9(11)
N2–Ru–N4	99.2(4)	Ru–N1–O1	178.9(10)	C4–N5–Ru	108.2(8)
		Hydrogen bonds[b)]			
N2–Cl1(A)	3.31(1)	N3–Cl3(A)	3.32(1)	N5–Cl1(E)	3.26(1)
N2–Cl3(B)	3.19(1)	N4–Cl2(A)	3.20(1)	N5–Cl3(A)	3.16(1)
N3–Cl2(C)	3.25(1)	N4–Cl3(D)	3.26(8)	O2–Cl2(F)	2.916(9)
		trans-[RuCl(en)$_2$NO]Cl$_2$ (**3**)			
Ru–Cl1	2.341(9)	Ru–N5	2.109(4)	N5–C4	1.492(5)
Ru–N1	1.779(8)	O–N1	1.098(6)	C1–C2	1.507(8)
Ru–N2	2.103(4)	N2–C1	1.483(5)	C3–C4	1.503(8)
Ru–N3	2.098(3)	N3–C2	1.481(6)		
Ru–N4	2.111(3)	N4–C3	1.494(6)		
N1–Ru–Cl1	179.08(9)	N2–Ru–N5	174.8(1)	Ru–N2–C1	109.4(2)
N1–Ru–N2	93.8(2)	N3–Ru–Cl1	87.7(1)	N2–C1–C2	108.4(3)
N1–Ru–N3	92.1(2)	N3–Ru–N4	174.6(1)	C1–C2–N3	107.4(3)
N1–Ru–N4	93.3(2)	N3–Ru–N5	98.4(1)	C2–N3–Ru	109.5(2)
N1–Ru–N5	91.4(2)	N4–Ru–Cl1	87.0(2)	Ru–N4–C3	109.4(2)
N2–Ru–Cl1	87.0(2)	N4–Ru–N5	81.5(1)	N4–C3–C4	108.5(3)
N2–Ru–N3	81.4(1)	N5–Ru–Cl1	87.8(2)	C3–C4–N5	107.2(3)
N2–Ru–N4	98.3(1)	Ru–N1–O	177.7(3)	C4–N5–Ru	108.1(3)
		Hydrogen bonds[c)]			
N2–Cl2(A)	3.29(1)	N3–Cl2(C)	3.248(6)	N4–Cl3(A)	3.186(8)
N2–Cl2(B)	3.310(9)	N3–Cl3(D)	3.27(1)	N5–Cl3(D)	3.398(8)
		trans-[Ru(NCS)(en)$_2$NO](NCS)$_2$ (**4**)			
Ru–N1	1.85(1)	O–N1	1.14(2)	S1–C3	1.55(2)
Ru–N2	2.17(1)	N2–C1	1.50(2)	C3–N4	1.15(2)
Ru–N3	2.04(1)	N3–C2	1.47(2)	S2–C4	1.636(9)
Ru–N4	1.89(1)	C1–C2	1.50(3)	C4–N5	1.15(1)
N1–Ru–N2	88.7(4)	N2–Ru–N2′	93.1(4)	C1–C2–N3	108.3(16)
N1–Ru–N3	90.5(4)	N2–Ru–N3′	174.6(4)	C2–N3–Ru	112.4(10)
N1–Ru–N4	174.6(7)	N3–Ru–N3′	103.8(4)	Ru–N4–C3	176.8(15)
N2–Ru–N3	81.6(4)	Ru–N1–O	175.2(15)	N4–C3–S1	172.1(17)
N2–Ru–N4	87.7(4)	Ru–N2–C1	106.1(8)	N5–C4–S2	176.3(16)
N3–Ru–N4	92.8(4)	N2–C1–C2	108.7(15)		
		Hydrogen bonds[d)]			
N2–S2(A)	3.36(1)	N3–S2(A)	3.30(1)		
N2–N5(B)	3.03(2)	N3–N5(C)	2.94(2)		

a) Key to symmetry operation; A: x, y, z; B: x, $-y+1$, $z+1/2-1$. b) Key to symmetry operation; A: x, y, z; B: $-x$, $-y$, $z+1/2-1$; C: $x+1/2$, $-y+1/2$, z; D: x, $y+1$, z; E: $-x+1/2$, $y+1/2-1$, $z+1/2$; E: x, $y-1$, z; F: $x+1/2$, $-y+1/2$, z. c) Key to symmetry operation; A: x, y, z; B: $-x+1/2$, $-y+1/2+1$, $z+1/2$; C: $x+1/2-1$, $-y+1/2$, $-z$; D: $x+1/2-1$, $-y+1/2$, $-z+1$. d) Key to symmetry operation; A: $-x+1/2$, $-y$, $z+1/2$; B: x, $y+1$, z; C: x, y, z.

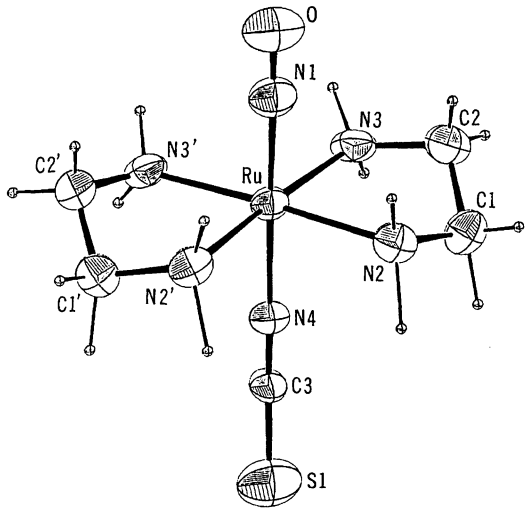

Fig. 4. ORTEP drawing and atomic numbering scheme of *trans*-$[Ru(NCS)(en)_2NO]^{2+}$ (**4**).

are in general positions. However, the $\delta\lambda$ conformation is either in **2** or **3**. Generally, the conformation of the ethylenediamine rings in *trans*-type octahedral bis(ethylenediamine) complexes is known to be $\delta\lambda$, with only a few exceptions.[14,15] Although the complex cation **3** does not essentially show optical activity, all of the atoms are in a spiral arrangement in the crystal lattice. Thus, chirality arises from the hydrogen bonds between the amine hydrogens and the chloride ions in the lattice. The crystal structure is shown in Fig. 5. In all of the other crystals, the hydrogen bonds were observed as well as in **3**.

In all of the complex cations, the NO is essentially linear with the ruthenium atom, and the Ru–NO and N–O bond lengths are similar to the typical values in other

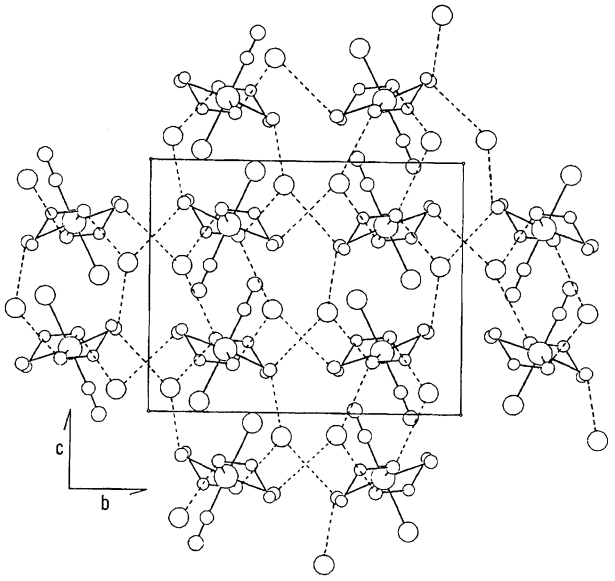

Fig. 5. The crystal structure of *trans*-$[RuCl(en)_2NO]$-Cl_2 (**3**) projected along the *a* axis. The dotted lines indicate hydrogen bonds.

$\{Ru^{II}–NO^+\}$-type complexes.[1—3,16—24] In the complex cation of **1**, the bond lengths of O1–N1, N1–Ru, and Ru–O2 and the angles of O1–N1–Ru and N1–Ru–O2 are comparable to those in *trans*-$[Ru(OH)L_4NO]^{2+}$ (L=NH_3,[23] py,[24] or 1/2 bpy;[25] py=pyridine, bpy=2,2′–bipyridine).[26] On the other hand, **3** has a longer Ru–Cl bond length and a greater linearity of the Cl–Ru–N–O axis than do those of *trans*-$[RuClL_4NO]^{2+}$, where L=py[27] and 1/2 bpy,[28] though the N–O bond of **3** is longer than those of the latter complexes.[29] The py and bpy ligands act as a π-acceptor on coordination and the nature of the ligands influences the X–Ru–N–O bond (X=OH or Cl), although the L is in a position *cis* to the moiety. Because the OH ligand is stronger σ- and π-donors than the Cl ligand, a direct interaction between the OH and RuNO moieties is stronger than that between the Cl and RuNO moieties. Thus, in hydroxo complexes, no difference in the bond lengths and angles caused by the L was found in O–Ru–N–O; however in the chloro complexes a difference was found.

The Ru–O2 bond in **1** is significantly shorter than that of **2**, indicating that the OH ligand is stronger than the OH_2 ligand as a π-donor.

In the $[RuX(en)_2NO]^{2+}$ complexes, the N–O bond becomes shorter in the order of OH, NCS, and Cl, and the Ru–N–O angle also becomes larger in the same order, reflecting that the π-donor ability of X becomes stronger in the order Cl, NCS, and OH, as shown in the IR discussion.[9]

Structures of the *cis* Complexes. ORTEP drawing of the complex cations of **5** and **7** are shown in Figs. 6 and 7, respectively, and the selected bond lengths and angles of **5**, **6**, and **7** are listed in Table 5. In these complex cations, the two ethylenediamine rings are situated in a position *cis* to each other and ligand X (X=Cl, Br, or NCS) is also situated in a position *cis* to NO. This supports the results for the IR, UV-vis, and NMR spectra as well as in the *trans* complexes.[9] The space groups of **5** and **6** are $P2_1/a$ and the symmetry center does not exist on the atoms. Therefore, a pair

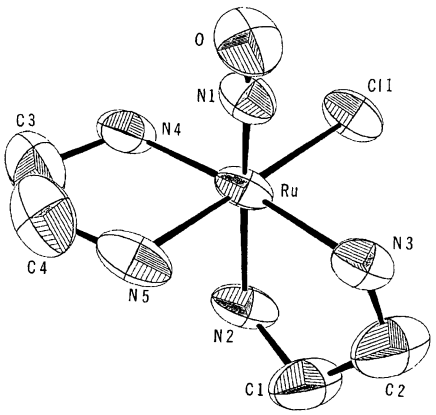

Fig. 6. ORTEP drawing and atomic numbering scheme of *cis*-$[RuCl(en)_2NO]^{2+}$ (**5**).

Table 5. Selected Bond Lengths (Å) and Angles (°) with Their Estimated Standard Deviations in Parentheses of The *cis* Complexes

		cis-[RuCl(en)$_2$NO]ClPF$_6$ (**5**)			
Ru–Cl1	2.365(2)	Ru–N5	2.097(6)	N5–C4	1.42(1)
Ru–N1	1.757(7)	O–N1	1.13(1)	C1–C2	1.45(1)
Ru–N2	2.101(7)	N2–C1	1.48(1)	C3–C4	1.46(2)
Ru–N3	2.108(5)	N3–C2	1.50(1)		
Ru–N4	2.085(5)	N4–C3	1.44(1)		
N1–Ru–Cl1	96.4(2)	N2–Ru–N5	87.0(3)	Ru–N2–C1	110.3(5)
N1–Ru–N2	174.5(2)	N3–Ru–Cl1	88.2(2)	N2–C1–C2	111.4(9)
N1–Ru–N3	94.6(3)	N3–Ru–N4	170.7(3)	C1–C2–N3	109.7(7)
N1–Ru–N4	94.7(3)	N3–Ru–N5	98.0(2)	C2–N3–Ru	111.4(5)
N1–Ru–N5	90.9(3)	N4–Ru–Cl1	91.0(2)	Ru–N4–C3	112.2(6)
N2–Ru–Cl1	86.4(2)	N4–Ru–N5	81.7(2)	N4–C3–C4	113.5(9)
N2–Ru–N3	80.7(2)	N5–Ru–Cl1	170.1(2)	C3–C4–N5	116.0(8)
N2–Ru–N4	90.0(2)	Ru–N1–O	176.6(6)	C4–N5–Ru	110.3(5)
		Hydrogen bonds[a)]			
N2–Cl2(A)	3.315(6)	N2–Cl2(B)	3.238(6)	N3–Cl3(C)	3.109(6)
		cis-[RuBr(en)$_2$NO]BrPF$_6$ (**6**)			
Ru–Br1	2.489(3)	Ru–N5	2.16(2)	N5–C4	1.46(3)
Ru–N1	1.73(2)	O–N1	1.11(3)	C1–C2	1.49(4)
Ru–N2	2.12(2)	N2–C1	1.48(3)	C3–C4	1.35(5)
Ru–N3	2.15(2)	N3–C2	1.44(4)		
Ru–N4	2.14(2)	N4–C3	1.49(4)		
N1–Ru–Br1	94.0(6)	N2–Ru–N5	88.9(10)	Ru–N2–C1	111.8(16)
N1–Ru–N2	172.0(6)	N3–Ru–Br1	88.0(5)	N2–C1–C2	108.4(25)
N1–Ru–N3	96.9(9)	N3–Ru–N4	170.2(9)	C1–C2–N3	111.7(22)
N1–Ru–N4	92.9(9)	N3–Ru–N5	98.3(8)	C2–N3–Ru	111.8(16)
N1–Ru–N5	90.1(10)	N4–Ru–Br1	91.8(6)	Ru–N4–C3	108.4(18)
N2–Ru–Br1	87.6(5)	N4–Ru–N5	81.1(1)	N4–C3–C4	118.4(32)
N2–Ru–N3	78.9(8)	N5–Ru–Br1	172.0(6)	C3–C4–N5	118.9(26)
N2–Ru–N4	91.3(8)	Ru–N1–O	178.8(19)	C4–N5–Ru	109.8(16)
		cis-[Ru(NCS)(en)$_2$NO]I$_2$·H$_2$O (**7**)			
Ru–N1	1.751(8)	Ru–N6	2.043(8)	N5–C4	1.51(1)
Ru–N2	2.107(8)	O1–N1	1.13(1)	C1–C2	1.49(2)
Ru–N3	2.109(8)	N2–C1	1.46(2)	C3–C4	1.48(2)
Ru–N4	2.104(8)	N3–C2	1.51(1)	N6–C5	1.14(1)
Ru–N5	2.093(8)	N4–C3	1.50(2)	C5–S	1.62(1)
N1–Ru–N2	173.2(4)	N3–Ru–N4	170.2(3)	C1–C2–N3	107.4(9)
N1–Ru–N3	93.7(3)	N3–Ru–N5	97.3(3)	C2–N3–Ru	112.5(6)
N1–Ru–N4	96.1(4)	N3–Ru–N6	87.1(3)	Ru–N4–C3	109.0(6)
N1–Ru–N5	91.9(3)	N4–Ru–N5	81.6(3)	N4–C3–C4	109.1(9)
N1–Ru–N6	95.3(4)	N4–Ru–N6	92.7(3)	C3–C4–N5	107.1(9)
N2–Ru–N3	79.8(3)	N5–Ru–N6	171.3(3)	C4–N5–Ru	109.6(6)
N2–Ru–N4	90.4(3)	Ru–N1–O1	175.9(8)	Ru–N6–C5	166.4(8)
N2–Ru–N5	87.2(3)	Ru–N2–C1	110.3(6)	N6–C5–S	178.0(9)
N2–Ru–N6	86.2(3)	N1–C1–C2	110.1(9)		
		Hydrogen bonds[b)]			
O2–I1(A)	3.513(8)		N5–I1(C)	3.676(8)	
O2–I2(B)	3.563(8)		N5–I2(D)	3.508(8)	

a) Key to symmetry operation; A: $x+1/2-1$, $-y+1/2-1$, z; B: $-x-1/2+1$, $-y-1/2+1$, $-z+1$; C: $-x+1$, $-y$, $-z+1$. b) Key to symmetry operation; A: $x+1/2+1$, $-y+1/2-1$, z; B: $x+1/2+1$, $-y+1/2$, $-z-1$; C: $-x+1/2+1$, $-y+1$, $z+1/2$; D: x, y, z.

of enantiomers exist in the lattices; the Δ-form of the complex cation of **5** is shown in Fig. 6. The crystals of **5** and **6** were isomorphous to each other. On the other hand, **7** resolved spontaneously, and the absolute configuration was Δ (Fig. 7). In the complex cations of **5** and **6**, the en ring, whose ligating atoms are N4 and N5, is *lel* and another is *ob*. In **7**, the former is *ob* and the latter is *lel*. These suggest that the NO ligand

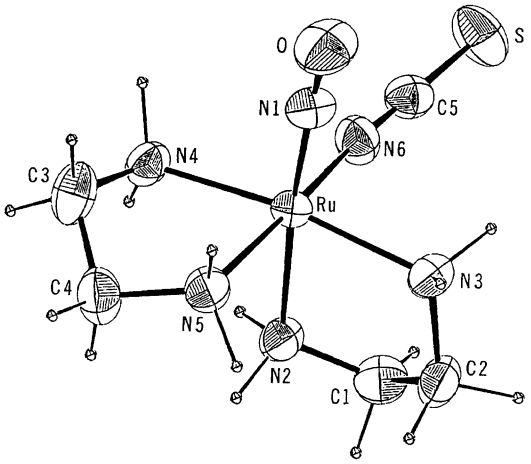

Fig. 7. ORTEP drawing and atomic numbering scheme of *cis*-$[Ru(NCS)(en)_2NO]^{2+}$ (**7**).

does not influence the gauche conformation of the en ligands. Because ligand X (X=Cl, Br, or NCS) does not also influence the conformation, the conformation seems to occur incidentally, though the *lel·ob* or *ob·lel* combination is stabler than other conformations. In all of the crystals of the *cis* complexes, the hydrogen bonds were observed as well as in those of the *trans* complexes.

All of the *trans* and *cis* complex cations are of a slightly distorted octahedron, and the Ru atom is displaced toward the NO group out of the best plane, consisting of the four atoms in positions *cis* to the NO.[30] The displacements are as follows: **1**, 0.04(2); **2**, 0.151(6); **3**, 0.098(2); **4**, 0.014(6); **5**, 0.155(3); **6**, 0.13(1); **7**, 0.155(4) Å. This displacement is smaller in the *trans* complex than in the *cis* complex, except for **2**. Because the displacement is caused by a steric hindrance between the bulky RuNO bond orbital and the ligands in positions *cis* to the NO, it is reasonable that the larger displacement is found in the *cis* complex in which larger X (X=Cl, Br, or NCS) than the NH_2 moiety of the en is situated at a position *cis* to NO. The bite angles of the en ligands in the *trans* complexes (81.7(7) for **1**, 81.6(5) and 81.9(4) for **2**, 81.4(1) and 81.5(1) for **3**, and 81.6(4)° for **4**) are equal to those of the en ligand which is situated on a position *cis* to the NO in the *cis* complexes (81.7(2) for **5**, 81.1(1) for **6**, and 81.6(3)° for **7**); these are larger than those of another ring in the *cis* complexes: (80.7(2) for **5**, 78.9(8) for **6**, and 79.8(3)° for **7**). These rings are hindered by the NO and X or en. Thus, the smaller displacement in the *trans* complex can be explained, except for **2**. For **2**, because the aqua ligand is smaller than the X (X=OH, Cl, and NCS), and the Ru–OH_2 bond length is longer than Ru–X, the displacement becomes larger, even though the interference still remains.

In **4** and **7**, the NCS ligand was found to coordinate to the ruthenium through the nitrogen atom. These facts support the validity for our previous determination based on the ^{14}N NMR spectra.[9] Structural information concerning the three NCS ions was obtained: Although the N–C bond lengths are equal in all of the NCS groups, the C–S bond length of the *trans* isomer is shorter than that of the *cis* isomer, which is comparable to that of the counter anion of the *trans* isomer **4**, and the N–C–S bond angle of the *trans* isomer is smaller than those of the *cis* isomer and the uncoordinated ion. This difference would be related to a difference in the π-interaction of the Ru–N bond. A significant difference between the *trans* and *cis* isomers was also observed regarding the Ru–N–C angles, which was caused by the steric hindrance mentioned above.

***trans*-Strengthening Effect.** The structures of two pairs of *trans* and *cis* isomers for $[RuX(en)_2NO]^{2+}$ (X=Cl or NCS) were determined. In these pairs, the Ru–X (*trans* to the NO) bond lengths (2.341(9) Å for X=Cl and 1.89(1) Å for X=NCS) are significantly shorter than the Ru–X (*cis* to the NO) (2.365(2) Å for X=Cl and 2.043(8) Å for X=NCS), respectively. This *trans*-strengthening effect is well-known in $\{Ru^{II}–NO^+\}$-type complexes, which is explained by both σ- and π-bonding interactions of the NO with the ligand *trans* to the NO through the Ru.[1,19,20,31—33] On the other hand, all of the Ru–N (en) bond lengths in the *cis* isomers are almost equal to each other, and are also comparable to those of the *trans* isomers. Thus, no *trans*-strengthening effect was found in Ru–N (en). Also, no sterical hindrance was found around the en ligand in a position *trans* to NO. Therefore, this result indicates that the effect does not influence the ligands, which behave only as a σ-donor, even if the ligand is *trans* to NO.

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30) Equations of weighted best planes; $0.0(2)\ X-6.35(7)\ Y-5.6(1)\ Z=-2.66(2)$ for **1**, $-14.39(2)\ X-2.75(3)\ Y-1.83(4)\ Z=-2.76(1)$ for **2**, $-1.55(1)\ X-5.23(1)\ Y-8.831(5)\ Z=-3.783(3)$ for **3**, $0.000(4)\ X+5.52(2)\ Y-5.23(3)\ Z=-1.26(2)$ for **4**, $-9.19(2)\ X-2.02(2)\ Y+8.12(1)\ Z=0.94(1)$ for **5**, $-9.74(5)\ X-2.53(8)\ Y+7.79(3)\ Z=0.56(4)$ for **6**, and $-2.97(2)\ X-14.27(4)\ Y+5.23(2)\ Z=0.33(1)$ for **7**.
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