The Electronic Structure of Ru(III)–Ammine Complexes and the Product Distribution from Solid-state Thermal Reaction

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INDO-type UHF-MO calculations were carried out for Ru(III)–ammine complexes in order to investigate their electronic structures and bonding nature. It was revealed that the ground state of $RuX(NH_3)_5^{2+}$($X=F$, Cl, Br, or I) is the ^2E state and that that of *cis*-$RuX_2(NH_3)_4^+$ is the $^2A_1$ state; in $RuX(NH_3)_5^{2+}$, the odd electron exists not on the d_{xy} orbital but on the d_{xz} or d_{yz} orbital which interacts with the p_π orbital of the halide ligand, and in *cis*-$RuX_2(NH_3)_4^+$, this electron exists not on the d_{xz} or d_{xy} orbital but on the d_{yz} orbital which interacts with the p_π orbitals of the two halide ligands. Concenring the bonding nature, the following results were obtained: (1) the strength of the Ru–NH_3 bond in these complexes increases in the order, *cis*-$RuX_2(NH_3)_4^+ < RuX(NH_3)_5^{2+} < Ru(OH_2)(NH_3)_5^{3+} < Ru(NH_3)_6^{3+}$; (2) in the aqua-ammine complex, the Ru–OH_2 bond is weaker than the Ru–NH_3 bond; and (3) in the halogeno-ammine complexes, the *trans*-Ru–NH_3 bond is weaker than the *cis*-Ru–NH_3 bond. MO calculations were also carried out for some distorted states of $RuCl(NH_3)_5^{2+}$. From these results, a discussion is presented on the relation between the thermal reaction product and the reaction mechanism; *cis*-$RuCl_2(NH_3)_4^+$ is expected to be produced *via* an associative reaction mechanism, while the *trans*-form product is expected to result from a dissociative mechanism.

It is known that the ammine or aqua ligand of Ru(III)–ammine complexes can be substituted for the outer-sphere halide ion *via* a solid-state thermal (30—210 °C) reaction.[1–3] This reaction is interesting from the viewpoint of the synthesis of certain Ru(III)–ammine complexes, because the halide ligand is substituted for the water molecule in the aqueous solution, while the ammine or aqua ligand is substituted for the halide ion. It has been suggested that the main product of this monohalogenopentaammine complex reaction is the *cis*-dihalogenotetraammine complex,[4] although the *trans*-form is expected as the main product due to the fact that the *trans*-effect of the halide ligand is greater than that of the ammine ligand. In order to clarify the reason why this reaction gives a *cis*-form product, not only experimental results, but also theoretical work are necessary, since calculations can give meaningful information about the electronic structure and the bonding nature of these complexes. Although some experimental work, such as UV-VS spectroscopic and ESR studies have been reported, only a few studies of MO calculations have been published on these complexes.[5,6]

In this work, a semi-empirical UHF-MO study was carried out for the hexaammine-, aquapentaammine-, monohalogenopentaammine-, and *cis*-dihalogenotetraammine–ruthenium(III) complexes. A discussion is presented on thier electronic structures, including electron configuration, the bond strength between metal and ligand, and the *trans*-effect of the ligand. From the results of MO calculations on the distorted state, which is considered to be a thermally-excited state, a discussion is presented on the reaction products and the mechanism of the solid-state thermal-substitution reaction.

Calculations and Geometries

Calculations. The method used here is the INDO-type UHF-MO method, which has been presented in detail elsewhere.[7] The resonance integrals were evaluated by means of the Wolfsberg-Helmholz approximation.[8] For the Ru and Rh atoms, the valence-state ionization potentials, I_μ, were evaluated from atomic spectra.[9] One-center Coulomb-repulsion integrals, $\gamma_{\mu\mu}$, were taken from the work of Di Sipio *et al.*[10] Two-center Coulomb-repulsion integrals were approximated using a modification of the Ohno equation.[11,12] For the atoms of the ligand, the values of I_μ were taken from the Hinze and Jaffé work,[13] and those of $\gamma_{\mu\mu}$ were estimated from the same work using the Pariser-Parr approximation.[14] A double-ζ type d-orbital was used for the 4d orbitals of the Ru and Rh atoms,[15] while single Slater-type orbitals[16,17] were used for all s and p orbitals. The quantity, E_{AB}, is used as the bond index, which gives the energy contribution of the AB bond to the total energy. Thus, a large absolute value of E_{AB} indicates a strong interaction between atoms A and B.[18,19]

Geometries. The Rh–Cl bond length is taken to be 2.50 Å from that corresponding to $RhCl_6^{3-}$,[20] and that of Rh–Br is estimated to be 2.6475 Å. The geometries of (a) $RuX(NH_3)_5^{2+}$, (b) $Ru(OH_2)(NH_3)_5^{3+}$, and (c) *cis*-$RuX_2(NH_3)_4^+$($X=F$, Cl, Br, and I) are shown in Fig. 1. The Ru–N and Ru–O interatomic distances are taken to be 2.23 and 2.50 Å from the corresponding values for $[Ru(OH)(NO)(NH_3)_4]Cl_2$,[21] respectively. The Ru–Cl bond length is taken to be 2.40 Å from the corresponding value of the similar $[RhCl(NH_3)_5]Cl_2$.[22] The Ru–F, Ru–Br, and Ru–I bond lengths are estimated to be 2.115, 2.5475, and 2.7191 Å, respectively. For all the complexes, the geometries of the ammine and aqua ligands are taken to be those of free molecules.[23]

Results and Discussion

Parametrization. In order to determine the values of the Wolfsberg-Helmholz parameter, K, MO calculations were carried out for $RhCl_6^{4-}$ and $RhBr_6^{4-}$, since the electronic structures of these complexes have been investigated in detail. The calculated spin densities on the ligand are given in Table 1, together with experimental values.[24] All the calculations give rather rea-

TABLE 1. EFFECTS OF K VALUES IN INDO-TYPE UHF-MO CALCULATIONS OF RhX_6^{4-}

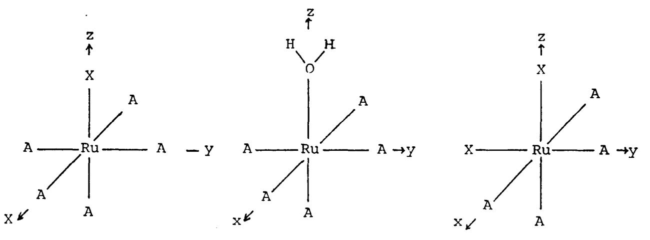
Compound	$RhCl_6^{4-}$						$RhBr_6^{4-}$			
Calculation	I[a]	II[a]	III[a]	IV[b]	V[b]	Obsd[c]	I[a]	II[a]	III[b]	Obsd[c]
K	0.50	0.60	0.70	0.50	0.70		0.50	0.70	0.70	
Spin fraction										
f_s (%)	0.71	0.94	1.18	0.73	1.21	1.1	0.54	0.91	0.96	1.2
$f_{p\sigma}$ (%)	2.88	3.52	4.11	3.13	4.54	8.6	2.85	4.12	4.64	9.5

a) The AO exponents of Richardson *et al.* were used. b) The AO exponts of Basch and Gray were used. c) Ref. 24.

TABLE 2. COMPARISON BETWEEN THE TOTAL ENERGIES, ELECTRON DENSITIES, AND THE d_π-p_π BONDING INTERACTION OF CONFIGURATIONS I AND II

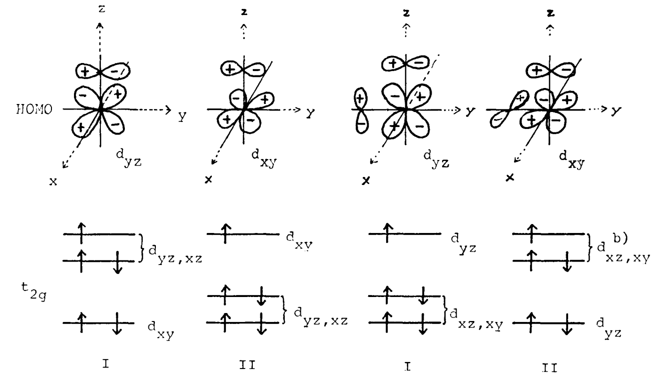
Compound	$RuCl(NH_3)_5^{2+}$		*cis*-$RuCl_2(NH_3)_4^+$	
Configuration[a]	I	II	I	II
Total energy (eV)	−2148.06	−2147.83	−2202.97	−2201.38
Electron density (e)				
Ru { d	6.234	6.201	6.252	6.246
Ru { s, p	1.098	1.112	1.135	1.132
Cl	7.368	7.434	7.432	7.447
cis-NH_3	7.656	7.639	7.667	7.667
trans-NH_3	7.675	7.698	7.703	7.678
E_{Ru-Cl} (eV)	−15.08	−14.31	−14.75	−14.37
$E^{(1)+(2)}_{d_\pi-p_\pi}$ (eV)	−1.21	0.0	− 0.99	− 0.55

a) See Fig. 2.



(a) $RuX(NH_3)_5^{2+}$ (b) $Ru(OH_2)(NH_3)_5^{3+}$ (c) *cis*-$RuX_2(NH_3)_4^+$

Fig. 1. Coordinate systems of Ru(III)-ammine complexes (A=NH_3 and X=F, Cl, Br, or I).



$RuX(NH_3)_5^{2+}$ *cis*-$RuX_2(NH_3)_4^+$

Fig. 2. Two types of electron configuration and the orbital interaction schemes[a] of $RuX(NH_3)_5^{2+}$ and *cis*-$RuX_2(NH_3)_4^+$. a) The d_π-p_π anti-bonding orbitals are shown here. The bonding orbitals are omitted, since the electron occupancy of these MO's are not different between the two types of electron configuration. b) The d_{xy}-p_{2x} interaction is given here. The d_{xz}-p_{1x} one is similar to this interaction.

sonable spin fractions, f_s, for both the Cl 3s-orbital and the Br 4s-orbital, while they give values that are too small for the spin fractions, $f_{p\sigma}$, of both the Cl $3p_\sigma$-orbital and the Br $4p_\sigma$-orbital. Calculation III (K= 0.70) appears to be the most reasonable, although the value of $f_{p\sigma}$ is also too small. When orbital exponents of Basch and Gray[16] are used instead of those of Richardson *et al.*,[15] the results for f_s and $f_{p\sigma}$ improve slightly. These results do not appear to be unreasonable, since a large uncertainty may be included in experimental spin fraction. From these calculations, the empirical parameter K was taken to be 0.70 and Basch and Richardson orbital exponents were used in the UHF-MO calculation.

Electron Configuration. Ru(III) complexes have a low-spin d^5 electron configuration. As is shown in Fig. 2, there are two possibilities: the complexes may be of configuration I or II. For $RuX(NH_3)_5^{2+}$(X=Cl and Br), Verdonck and Vanqickenborne[5] have suggested that configuration I is reasonable. Kaplan and Navon[6] have also reported from their ESR study of $RuX(NH_3)_5^{2+}$ (X=Cl and Br) that the d_{xz} and d_{yz} orbitals are unstable relative to the d_{xy} orbital. Unfortunately no theoretical interpretation has been reported on this issue. Thus, it is necessary to theoretically ascertain the orbital order.

In the present work, an investigation was made to determine which configuration, I or II, are the ground states of $RuCl(NH_3)_5^{2+}$ and *cis*-$RuCl_2(NH_3)_4^+$. As is shown in Table 2, configuration I has a lower total energy than configuration II by *ca.* 0.23 eV for the former complex and by *ca.* 1.6 eV for the latter.

TABLE 3. ELECTRON DISTRIBUTION AND BOND STRENGTH OF Ru(III)-AMMINE COMPLEXES

Compound	$RuX(NH_3)_5^{2+}$				*cis*-$RuX_2(NH_3)_4^+$				$RuX(NH_3)_5^{3+}$	
	F	Cl	Br	I	F	Cl	Br	I	NH_3	H_2O
Electron density (e)										
Ru d	6.137	6.234	6.261	6.278	6.085	6.252	6.287	6.318	6.226	6.146
Ru s, p	0.971	1.098	1.119	1.148	0.888	1.135	1.175	1.219	1.148	0.948
X	7.607	7.368	7.316	7.262	7.632	7.432	7.389	7.349	—	7.822
cis-NH_3	7.653	7.656	7.657	7.659	7.684	7.667	7.684	7.686	7.604	7.622
trans-NH_3	7.675	7.675	7.674	7.670	7.698	7.703	7.695	7.696	7.604	7.596
Net charge										
Ru	0.892	0.668	0.620	0.574	1.027	0.613	0.538	0.643	0.626	0.906
E_{AB} (eV)										
cis-Ru-NH_3	−10.43	−10.64	−10.69	−10.68	− 9.90	−10.34	−10.63	−10.56	−13.33	−10.61
trans-Ru-NH_3	−10.40	−10.47	−10.47	−10.33	−10.16	−10.33	−10.40	−10.41	−13.33	−11.02
Ru-X	−15.49	−15.26	−13.60	−12.78	−15.89	−14.75	−13.03	−12.35	—	− 5.75

To investigate the reason why configuration I is the ground state, the E_{Ru-Cl} value of that configuration are compared with that of configuration II for $RuCl(NH_3)_5^{2+}$ in Table 2. The absolute value of E_{Ru-Cl} is greater for configuration I (−15.08 eV) than for II (−14.31 eV), which suggests that the stability of these two electron configuration depends largely on the Ru–Cl bond strength.[25] In more detail, a large difference is found not between $E_{d\pi-sp\sigma}$ and $E_{p\pi-p\pi}$ but for $E_{d\pi-p\pi}$ of E_{Ru-Cl}; in configuration I ($E_{d\pi-p\pi}=-1.21$ eV), the halogen donates a p_π-electron to the d_π-orbital of the metal ion, since the d_π-orbital of the Ru atom has only one electron and is able to accept electrons from the ligand. On the other hand, the halogen cannot donate an electron in configuration II ($E_{d\pi-p\pi}=0.0$ eV), since the d_π-orbital interacting with the halogen-atom p_π-orbital is filled. The difference between the $E_{d\pi-p\pi}$ values for configurations I and II is almost the same as the difference of between their total E_{Ru-Cl} values. Thus, the d_π-p_π bonding interaction between the Ru and Cl atoms stabilizes configuration I. For *cis*-$RuCl_2(NH_3)_4^+$, the same results were obtained, as is shown in Table 2; configuration I has two d_π-p_π interactions, while configuration II has only one, which makes configuration I more stable than II.

Therefore, the π-electrons of the halide ligand delocalize onto the d_π-orbital of the Ru atom in configuration I, while they cannot do so in configuration II. These results are reflected in the electron distributions of these complexes; the electron density of the p_π-orbital of the Cl atom is smaller in configuration I than in II. The d_π-orbital of the Ru atom, on the other hand, has more electrons in configuration I than does configuration II. It should be noted that the difference in electron density of the p_π-orbitals of the Cl atoms is almost the same as that of the electron density of the d_π-orbital of the Ru atom. In conclusion, the electron configuration in the ground state is I, which results from the interaction of the Cl-atom p_π-orbital with the half-occupied d_π-orbital of the Ru atom.

Electron Density and Bond Strength. The result for Ru(III)–ammine complexes are shown in Table 3. The electron densities of the Ru atom for these complexes increase in the order: $Ru(OH_2)(NH_3)_5^{3+} < Ru(NH_3)_6^{3+} < RuX(NH_3)_5^{2+} <$ *cis*-$RuX_2(NH_3)_4^+$. The electron numbers of the ammine ligand for these complexes decrease in the order *cis*-$RuX_2(NH_3)_4^+ > RuX(NH_3)_5^{2+} > Ru(OH_2)(NH_3)_5^{3+} > Ru(NH_3)_6^{3+}$; *i.e.*, the numbers of electrons transfered from the ammine ligand to the metal decrease in reverse order. The net charges of the Ru(III) ion decrease in the order: $Ru(OH_2)(NH_3)_5^{3+} > Ru(NH_3)_6^{3+} > RuX(NH_3)_5^{2+}(X=Br,I) >$ *cis*-$RuX_2(NH_3)_4^+(X=Cl,Br,I)$. For both halogeno ammine complexes, the electron densities of the 4d-orbital of the Ru atom increase in the order; fluoro < chloro < bromo < iodo, and the electron densities of the p_π-orbital of the halide ligand decrease in reverse order, which suggests that the d_π-p_π interactions increase in the forward order.

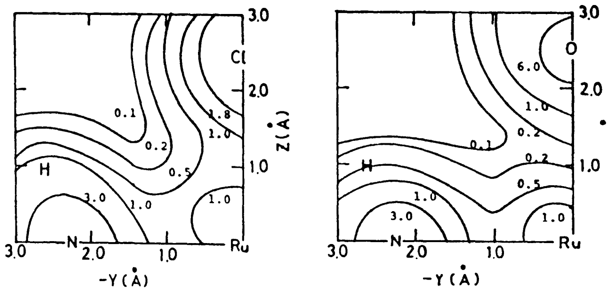
For both $RuX(NH_3)_5^{2+}$ and *cis*-$RuX_2(NH_3)_4^+$, the electron densities of the ammine, which is in the *cis*-position with respect to the halide ligand are smaller than those in the *trans*-position. Since the ammine ligand coordinates with the metal ion by donating its lone-pair electrons, it is expected that the *cis*-ammine coordinates more strongly with the Ru atom than the *trans*-ammine, which will be revealed in the following section on the basis of the E_{Ru-NH_3} value. In the aqua-complex, on the other hand, the electron density decreases for the ammine in *trans*-position more than for that in *cis*-position. From these results, it is conceivable that the *trans*-ammine coordination bond is stronger than that of the *cis*-ammine, which suggests that the aqua ligand has a weaker *trans*-effect than does the ammine ligand.

With the value of E_{AB} and electron-density contour maps, the bond strength of the Ru(III)–ligand can be investigated in more detail. The absolute values of E_{Ru-NH_3} for the complexes decrease in the order: $Ru(NH_3)_6^{3+} > Ru(OH_2)(NH_3)_5^{3+} > RuX(NH_3)_5^{2+} >$ *cis*-$RuX_2(NH_3)_4^+$ (see Table 3). It is of note that the Ru–NH_3 bond strength of $Ru(NH_3)_6^{3+}$ is the strongest of all these Ru(III)–ammine complexes. This result is in accord with the fact that the Ru–N stretching force constant of $Ru(NH_3)_6^{3+}$(2.01 mdyn/Å)[26] is the

TABLE 4. ELECTRONIC STRUCTURE OF THE DISTORTED STATE OF $RuCl(NH_3)_5^{2+}$

Structure[a)]	(1)	(2)	(3)	(4)[b)]
Electron density (e)				
Ru d	6.228	6.220	6.216	6.234
Ru s, p	1.096	1.096	1.092	1.098
cis-NH_3(1)	7.656	7.645	7.667	7.666
trans-NH_3	7.685	7.667	7.704	7.675
Cl	7.365	7.390	7.342	7.368
E_{AB} (eV)				
cis-Ru-NH_3(1)	−10.58	−10.93	−10.72	−10.41
trans-Ru-NH_3	−10.35	− 9.15	−10.17	−10.47
Ru-Cl	−15.07	−14.64	−15.27	−15.26
Total energy (eV)	−2148.12	−2148.13	−2151.59	−2148.06

a) Corresponing to Fig. 4. b) Ground-state structure.



(3-a) $RuCl(NH_3)_5^{2+}$ (3-b) $Ru(OH_2)(NH_3)_5^{3+}$

Fig. 3. Electron density contour maps.

largest of all these complexes (*ca.* 1.6—1.9 mdyn/Å for $RuX(NH_3)_5^{2+}$).[27)] The Ru–NH_3 bond strength in $Ru(OH_2)(NH_3)_5^{3+}$ is almost the same as those in halogeno ammine complexes, while the Ru–OH_2 bond strength is rather weak (see the value of E_{Ru-OH_2}). A weak coordination bond of the aqua ligand is also expected from the small electron distribution between the Ru atom and the aqua ligand (see the density contour map of 0.2 e in Figs. 3a and b). For both monohalogeno and *cis*-dihalogeno ammine complexes, the Ru–NH_3 bond strength in the position *trans* to the halide ligand is weaker than in the position *cis* for all complexes by *ca.* 0.1—0.3 eV (see Table 3). These results suggest that the *trans*-effect of halide ligand is stronger than that of the ammine ligand.

Electronic Structures of Some Distorted State. As described above, the *cis*-ammine ligand coordinates with the Ru atom more strongly than does the *trans*-ammine ligand. It is unexpected that the *cis*-ammine ligand is mainly substituted for the outer-sphere halide ion in the solid-state thermal reaction in spite of the strong *cis*-Ru–NH_3 bond.[3,4)] In order to clarify this problem, an MO study was carried out on the distorted state of $RuCl(NH_3)_5^{2+}$, because the distortion is expected to occur in the thermally-activated state.

UHF-MO calculations were carried out on the following distorted states of $RuCl(NH_3)_5^{2+}$: those for which (1) the angle between the z-axis and the *trans*-Ru–NH_3 bond is 20°, (2) the angle between the z-axis and the *cis*-Ru–NH_3 bond is 70° and (3) 110°. All of these distortions were examined in the plane including mainly the unpaired electron (see Fig. 4). These results are given in Table 4, accompanied by the ground state

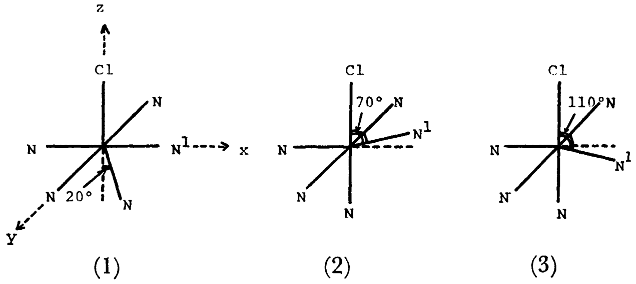


Fig. 4. Examined distorted states of $RuCl(NH_3)_5^{2+}$.

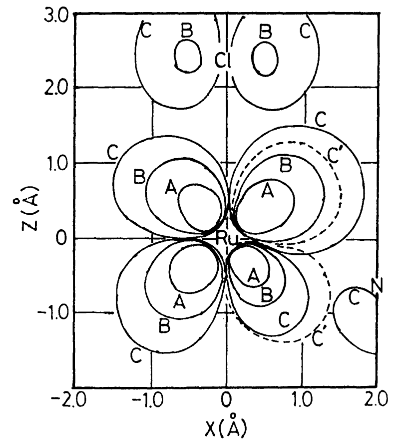


Fig. 5. LUMO contour map of $RuCl(NH_3)_5^{2+}$ (∠X–Ru–NH_3=110°, A=0.25e, B=0.05e, C=0.005e in distorted state and C′=0.005e in ground state).

result. In terms of the total energy, distorted state (3) is the most stable.[28)]

Thus, it is reasonable to conclude that the reaction mainly occurs from state (3). In the case of (3), the bent *cis*-Ru–NH_3 bond becomes stronger, while the *trans*-Ru–NH_3 bond becomes weaker. If the solid-state thermal-substitution reaction proceeds *via* a dissociative mechanism, the weak *trans*-Ru–NH_3 bond should dissociate to produce a complex with a *trans*-substituted structure.

The LUMO, which plays an important role in the nucleophilic attack, extends to the area between the bent Ru–NH_3 bond and the Ru–Cl bond more greatly than does that of non-distorted state, as is shown in Fig. 5. Thus, the nucleophilic attack of the outer-sphere anion is accelerated by the distortion, and the attack occurs in the direction is shown in Fig. 5. If the reaction proceeds *via* an associative mechanism, the entering group attacks the Ru atom in the direction in which the LUMO largely extends, followed by bond dissociation of the *trans*-Ru–NH_3 bond. Then, as the *cis*-ammine ligand transfers to the vacant position, the entering group transfers to the initial position of the *cis*-ammine ligand. Since the *cis*-substituted tetraammine complex is obtained as a main product,[4] the associative mechanism is expected to be the main reaction path in the thermal-substitution reaction of halogenopentaammine complexes in the solid state, which agrees with the negative values of the activated entropy for these reactions.

In conclusion, the present INDO-type UHF-MO study of Ru(III)–ammine complexes provides useful information about their electron configurations in the ground state and the bonding nature between the metal and ligand. Some other useful information has also been obtained with this method, which successfully suggests the relation between the distribution of the reaction products and the reaction mechanism. These results agree with experimental results.

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4) For example, $[RuCl(NH_3)_5]Cl_2$ gives $[RuCl_2(NH_3)_4]Cl$ in the solid-state thermal reaction. This reaction product has three Ru–N stretching bands at 483, 460, and 449 cm^{-1}. *cis*-$[RuCl_2(NH_3)_4]Cl$ has three Ru–N stretching bands at 480, 464, and 452 cm^{-1}, while *trans*-form one has only one band at 454 cm^{-1}. Thus, the reaction product appears to have a *cis*-form. (N. Iwasaki, S. Kohata, *et al.*, to be published.)

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28) This stabilization should be due to the Jahn-Teller effect, since the ground state is the ^2E state. Therefore, distortion is brought about not only by the thermal excitation, but also by the Jahn-Teller effect.