# Cis-Trans Isomerism among the Octahedral Diaquabis(*N,N*- or *N,N'*-dialkylethylenediamine)nickel(II) Complexes and Their Thermal Reaction Products

Yoshinori IHARA,† Yasuhiro SATAKE, Masatatsu SUZUKI, and Akira UEHARA*
Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi 1-1, Kanazawa 920
†Laboratory of Chemistry, Faculty of Education, Kanazawa University, Marunouchi 1-1, Kanazawa 920
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The thermochemical changes in coordination structure of diaquabis(*N,N*- or *N,N'*-dialkylethylenediamine)nickel(II) complexes ($[Ni(H_2O)_2(diamine)_2]X_2 \cdot nH_2O$) were reinvestigated by means of TG-DTA and electronic spectroscopy at room and elevated temperatures, where diamine is *N,N*- (or *N,N'*)-dimethylethylenediamine (*NN*- or *NN'*-dmen) or *N,N*-(or *N,N'*)-diethylethylenediamine (*NN*- or *NN'*-deen); X is $Cl^-$, $Br^-$, $I^-$, or $NO_3^-$; *n* is 0, 1, 2, or 3. The diaqua complexes prepared were all trans except for *cis*-$[Ni(H_2O)_2(NN\text{-dmen})_2]I_2$. The trans complexes with the symmetric (*N,N'*-dialkylsubstituted) diamines brought about a deaquation-anation upon heating, retaining the original trans configuration, while those with the asymmetric (*N,N*-dialkylsubstituted) diamines transformed into the cis complexes. In the case of the *NN*-dmen complexes, *cis*-halogenoaqua species were isolated as a stable intermediate during the thermal reactions. The complex nitrates changed to *trans*-dinitrato or *cis*-mononitrato species depending upon the diamines. The effects of the *N*-substituents in the diamines and of the anions on the patterns of thermal reactions were also discussed.

Nickel(II) complexes provide various informative examples of thermochromism in solid phase, which are mainly associated with a change in coordination geometry.[1] However, systematic knowledge is still lacking for the factors which govern the preference of particular coordination geometries at different temperatures.

We have studied the coordination structures of many bis(*N*- or *C*-substituted ethylenediamine)nickel(II) complexes and the products of their solid-phase thermal reactions, and the effects of *N*- or *C*-substituent group(s) upon their structural changes during the thermal treatment.[2–6] Our previous reports[2,3] clarified that the thermal reactions of the complexes containing *N,N*- or *N,N'*-dimethylethylenediamine (*NN*- or *NN'*-dmen) and *N,N*- or *N,N'*-diethylethylenediamine (*NN*- or *NN'*-deen) can be classified into either deaquation-anation(1) or deaquation(2) as shown below:

$$[Ni(H_2O)_2(diamine)_2]X_2\ (Oh) \xrightarrow{-2H_2O} [NiX_2(diamine)_2]\ (Oh') \quad (1)$$

$$[Ni(H_2O)_2(diamine)_2]X_2\ (Oh) \xrightarrow{-2H_2O} [Ni(diamine)_2]X_2\ (Sp) \quad (2)$$

where Oh (or Oh') and Sp represent octahedral and square planar species, respectively. Unfortunately, we were not able to decide whether the Oh and Oh' complexes are cis or trans in spite that the decision is fundamental for understanding the details of their thermal reactions.

The present study was therefore undertaken to reinvestigate the thermal reactions of the nickel(II) complexes containing the above four diamines especially for clarifying the details of cis-trans isomerism and the effects of *N*-substituents on the structural changes during the thermal reactions.

## Experimental

**Materials.** Four diamines (*NN*-dmen, *NN'*-dmen, *NN*-deen, and *NN'*-deen) of commercial reagent grade were used without further purification. The complexes, $[Ni(H_2O)_2(diamine)_2]X_2 \cdot nH_2O$ ($X=Cl^-$, $Br^-$, $I^-$, or $NO_3^-$; $n$=0, 1, 2, or 3), were prepared by the known methods.[7,8] The *NN*-deen complexes, $[Ni(NN\text{-deen})_2]X_2$ ($X=I^-$ and $NO_3^-$), were exclusively isolated as anhydrous square planar complexes.

**Measurements.** Electronic spectra in solid phase were measured by the diffuse reflectance method with a Hitachi U-3400 spectrophotometer. The spectra at elevated temperatures were monitored by use of a hand-made heating cell, which was set up on the apparatus and was controlled by a REX-C72 temperature controller equipped with a copper-constantan thermocouple. IR spectra were recorded on a JASCO A-3 spectrophotometer in Nujol mulls. The standardized cell for the apparatus was used for the IR spectral measurements at elevated temperatures. The measurements of TG-DTA and DSC were carried out with a Seiko TA station SSC 5000 apparatus under a constant flow of nitrogen ($0.2\ dm^3\ min^{-1}$ for TG-DTA; $0.03\ dm^3\ min^{-1}$ for DSC). Samples (10—20 mg) were triturated into fine powders beforehand, and were heated at the rate of $2.0\ ^\circ C\ min^{-1}$.

## Results

**Structures of $[Ni(H_2O)_2(diamine)_2]X_2 \cdot nH_2O$.** Diagnosis of cis and trans isomers of the bis(diamine)nickel(II) complexes has already been established by means of electronic spectroscopy.[9–11] The energy levels derived from F and P terms of a $d^8$ system ($Ni^{2+}$) in ligand fields of different symmetries (Oh, $D_{4h}$, and $C_{2v}$) are shown in Fig. 1, along with the rough sketches of the typical electronic spectra of *trans*- and *cis*-$[NiX_2(diamine)_2]$. In a $D_{4h}$ system, three or sometimes four bands are practically observed in visible-near IR region. The band due to $^3B_{1g} \rightarrow {}^3E_g$ (from $^3T_{1g}(F)$) transition is

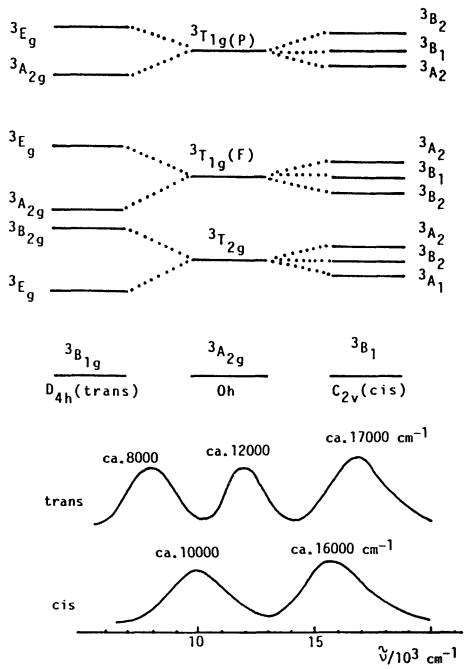



Fig. 1. Top: Energy level diagrams of a $d^8$ system in ligand fields of different symmetries. Bottom: Rough skeches of the electronic spectra of *trans*- and *cis*- $[NiX_2(diamine)_2]$.

normally observed at ca. 17000 cm$^{-1}$. The band of $^3B_{1g}\rightarrow{}^3A_{2g}$ (from $^3T_{1g}(F)$) transition seems to lie very close to that of $^3B_{1g}\rightarrow{}^3B_{2g}$ transition, giving one or two peaks around ca. 12000 cm$^{-1}$. The band at ca. 8000 cm$^{-1}$ is assigned to $^3B_{1g}\rightarrow{}^3E_g$ transition. On the other hand, in a $C_{2v}$ system, the splittings of the respective terms are close so that two rather broad bands are observed at ca. 16000 cm$^{-1}$ and ca. 10000 cm$^{-1}$.

Table 1 summarizes the spectral data of the diaqua complexes and the configurational assignments along with those of their thermal reaction products. At room temperature, only $[Ni(H_2O)_2(NN\text{-dmen})_2]I_2$ gives apparently a single band in near IR region, indicating that the complex belongs to cis configuration. All the other complexes show spectral patterns characteristic of trans geometry which gives three or four bands due to d–d transitions.

Chaudhuri et al. have pointed out[12] that the complex chloride and bromide with *NN*-dmen prepared by the same methods as ours are not the diaqua species, but *trans*-halogenoaqua ones, *trans*-$[NiX(H_2O)(NN\text{-dmen})_2]X\cdot nH_2O$ (X=Cl or Br), because the complexes behave as an 1 : 1 electrolyte in methanol ($\Lambda_m$=70 and 80 $\Omega^{-1}$ cm$^2$ dm$^{-3}$ for the chloride and bromide, respec-

Table 1. Electronic Spectral Data and Configurational Assignments

| Complex | Temp/°C | Band maxima, $\tilde{\nu}/10^3$ cm$^{-1}$ | | | | | | | Configuration |
|---|---|---|---|---|---|---|---|---|---|
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Cl_2\cdot 3H_2O$ | RT | 7.8 | | 12.0 (sh) | | 12.9 | | 17.1 | *trans*-Diaqua |
| | 110 | 8.0 | | | 12.9 | | | 16.9 | *trans*-Dichloro |
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Br_2\cdot H_2O$ | RT | 8.4 | | 12.3 | | 13.2 (sh) | | 17.4 | *trans*-Diaqua |
| | 80 | 7.4 | | | 12.8 | | | 16.9 | *trans*-Dibromo |
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]I_2\cdot 2H_2O$ | RT | 8.9 | | 12.4 | | 13.3 | | 17.7 | *trans*-Diaqua |
| | 60 | 6.9 | | 11.1 (sh) | | 12.6 | | 16.5 | *trans*-Diiodo |
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2](NO_3)_2\cdot 2H_2O$ | RT | 9.3 | | 12.0 | | 13.1 (sh) | | 17.4 | *trans*-Diaqua |
| | 60 | | 10.5 | | | | 17.0 | | *cis*-Mononitrato |
| | 130 | 8.5 | | 12.3 | | 13.3 | | 17.8 | *trans*-Dinitrato |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2]Cl_2\cdot H_2O$ | RT | 9.1 | | 12.1 | | 13.1 | | 17.6 | *trans*-Diaqua |
| | 60 | 8.3 | | 11.6 | | 12.6 | | 16.8 | *trans*-Dichloro |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2]Br_2$ | RT | 8.9 | | 12.1 | | 13.2 | | 17.4 | *trans*-Diaqua |
| | 100 | 7.5 | | | 13.3 | | | 16.2 | *trans*-Dibromo |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2]I_2$ | RT | 8.9 | | 12.5 | | 14.9 (sh) | | 17.5 | *trans*-Diaqua |
| | 100 | 7.0 | | | 11.8 | | | 16.1 | *trans*-Diiodo |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2](NO_3)_2$ | RT | 9.2 | | 12.1 | | 13.4 | | 17.5 | *trans*-Diaqua |
| | 90 | | 10.1 | | | | 17.0 | | *cis*-Mononitrato |
| *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2\cdot 2H_2O$ | RT | 8.1 | | 11.2 | | 13.2 | | 17.0 | *trans*-Diaqua |
| | 60 | | 9.5 | | | | 16.0 | | *cis*-Chloroaqua |
| | 95 | | 9.4 | | | | 15.9 | | *cis*-Dichloro |
| *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Br_2\cdot 2H_2O$ | RT | 8.3 | | 11.2 | | 13.2 | | 16.8 | *trans*-Diaqua |
| | 80 | | 9.5 | | | | 16.0 | | *cis*-Bromoaqua |
| | 95 | | 9.3 | | | | 15.7 | | *cis*-Dibromo |
| *cis*-$[Ni(H_2O)_2(NN\text{-dmen})_2]I_2$ | RT | | 9.9 | | | | 16.4 | | *cis*-Diaqua |
| | 90 | | | | | | | 20.0 | Square planar |
| *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2](NO_3)_2\cdot H_2O$ | RT | 8.6 | | 11.8 | | 13.4 (sh) | | 17.3 | *trans*-Diaqua |
| | 70 | 8.5 | | 11.5 | | 13.2 (sh) | | 17.1 | *trans*-Mononitrato |
| *trans*-$[Ni(H_2O)_2(NN\text{-deen})_2]Cl_2$ | RT | 7.4 | | | 10.2 | | | 16.4 | *trans*-Diaqua |
| | 100 | | 8.5 | | | | 14.9 | | *cis*-Dichloro |
| *trans*-$[Ni(H_2O)_2(NN\text{-deen})_2]Br_2$ | RT | 7.5 | | | 10.3 | | | 16.4 | *trans*-Diaqua |
| | 75 | | | | | | | 21.4 | Square planar |
| *trans*-$[Ni(H_2O)_2(en)_2](NO_3)_2$ | RT | 9.0 | | 12.7 | | 13.6 | | 18.3 | *trans*-Diaqua |
| | 70 | 8.8 | | 12.8 | | 13.6 | | 18.3 | *trans*-Dinitrato |
| | 170 | | 10.5 | | | | 17.5 | | *cis*-Mononitrato |

Table 2. Results of Thermal Analyses

| Complex | Dehydration | | Color | |
|---|---|---|---|---|
| | Temp/°C | Mass loss /% (calcd) | Room temp | After dehydration |
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Cl_2 \cdot 3H_2O$ | 25—75 | 22.79 (22.70) | Violet | Blue |
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Br_2 \cdot H_2O$ | 20—50 | 11.53 (12.00) | Violet | Blue |
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]I_2 \cdot 2H_2O$ | 25—45 | 12.72 (12.85) | Violet | Blue |
| *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2](NO_3)_2 \cdot 2H_2O$ | 30—58 | 16.58 (16.72) | Violet | Blue-violet |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2]Cl_2 \cdot H_2O$ | 20—58 | 12.73 (12.99) | Violet | Blue |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2]Br_2$ | 50—88 | 7.19 ( 7.40) | Violet | Blue |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2]I_2$ | 40—96 | 6.23 ( 6.20) | Violet | Green |
| *trans*-$[Ni(H_2O)_2(NN'\text{-deen})_2](NO_3)_2$ | 35—90 | 7.77 ( 7.99) | Violet | Blue |
| *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$ | 25—100 | 19.02 (19.06) | Violet | Blue-green |
| *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Br_2 \cdot 2H_2O$ | 20—100 | 15.24 (15.43) | Blue-violet | Blue-green |
| *cis*-$[Ni(H_2O)_2(NN\text{-dmen})_2]I_2$ | 20—83 | 7.12 ( 6.86) | Blue | Orange |
| *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2](NO_3)_2 \cdot H_2O$ | 25—53 | 12.96 (13.08) | Violet | Blue |
| *trans*-$[Ni(H_2O)_2(NN\text{-deen})_2]Cl_2$ | 55—100 | 8.97 ( 9.05) | Blue | Yellow-green |
| *trans*-$[Ni(H_2O)_2(NN\text{-deen})_2]Br_2$ | 30—84 | 7.34 ( 7.40) | Blue | Orange |
| *trans*-$[Ni(H_2O)_2(en)_2](NO_3)_2$ | 25—50 | 10.08 (10.63) | Violet | Violet |

tively). Indeed, our complex chloride with the same composition gave nearly the same molar conductivity (92 $\Omega^{-1}\,cm^2\,dm^{-3}$). However, the X-ray single-crystal analyses for the complex chloride[13] have revealed that the two water molecules undoubtedly occupy trans position in the octahedral environment. The low value in molar conductivity may be due to the contribution of chloroaqua species which are formed by deaquation-anation in methanol, because the violet powder slightly changed towards blue on dissolution, giving the spectrum whose peak maxima shift towards the red compared with that of the diaqua complex in solid state.

**Thermal Reactions of Complex Halides Containing Symmetric Diamines.** Table 2 summarizes the results of TG-DTA and the color changes upon dehydration of all the complexes. The TG-DTA curve of *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Cl_2 \cdot 3H_2O$ is shown in Fig. 2. The complex loses the five moles of waters (three lattice waters plus two coordinated waters) in one step at 25—75 °C, changing to the anhydrous complex. As shown in Fig. 3, the spectral pattern of the anhydrous product remains nearly unchanged in comparison with that of the original complex except that the red shifts of the

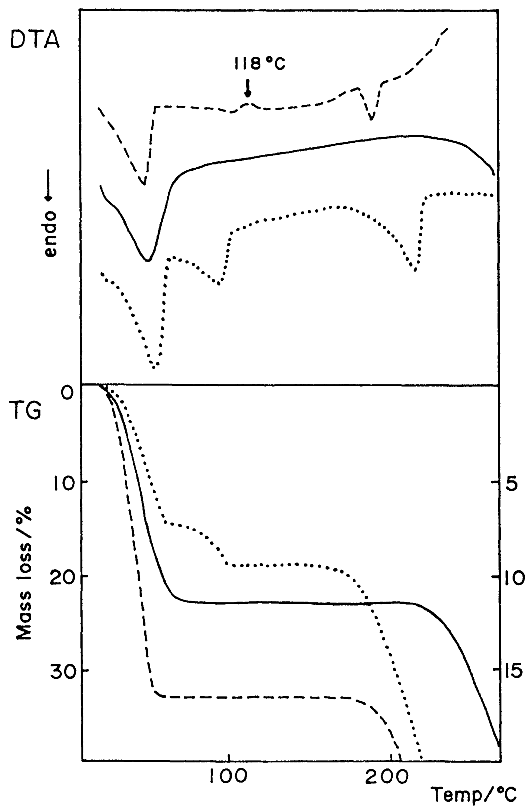



Fig. 2. TG-DTA curves for *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Cl_2 \cdot 3H_2O$ (——), *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$ (······), and *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2](NO_3)_2 \cdot 2H_2O$ (––––). The TG data of the last complex is illustrated against the right-hand axis.

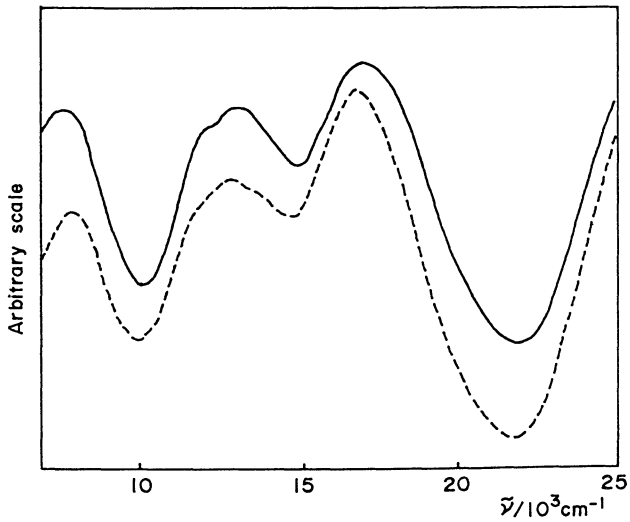



Fig. 3. Electronic spectra of *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Cl_2 \cdot 3H_2O$ (——) and the product obtained by heating the *trans*-complex at 110 °C (––––).

peak maxima take place because of the replacement of axial ligands ($H_2O \rightarrow Cl$). The remaining five complex halides with *NN'*-dmen and *NN'*-deen also liberate their waters below 100 °C, giving the stable anhydrous products with color changes, as summarized in Table 2. These products show three or four bands in their electronic spectra, indicating that the *trans*-octahedral configurations are still retained upon dehydration. It can thus be concluded that a simple deaquation-anation (*trans*-diaqua→*trans*-dianiono) occurs in all the complex halides with the symmetric diamines, retaining the original geometries.

**Thermal Reactions of Complex Halides Containing Asymmetric Diamines.** The *NN*-dmen or *NN*-deen complexes showed various patterns of thermal reactions depending on the anions. The TG-DTA curve of *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$ (Fig. 2) indicates that the complex dehydrates in two-steps. The violet diaqua complex loses three moles of water (two lattice waters plus one coordinated water) to become blue at 25—60 °C and then blue-green at 60—100 °C with evolution of the remaining one mole of coordinated water.

Figure 4 shows the electronic spectra of *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$, and the products obtained by heating the trans complex at 60 °C and 95 °C. As seen from the figure, both products display a spectral pattern characteristic of cis configuration. The corresponding bromide gives almost the same results in TG-DTA and spectral changes (Table 1). Accordingly, thermal reactions of the two complexes

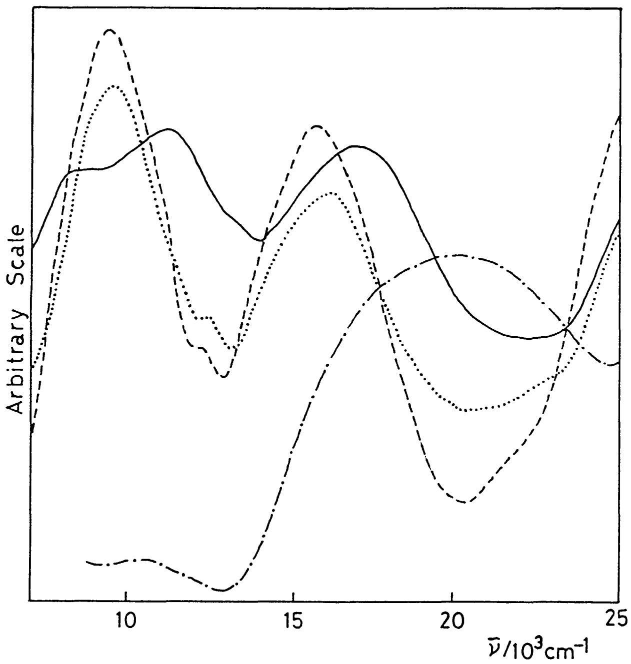



Fig. 4. Electronic spectra of *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$ (——), the products obtained by heating the *trans*-complex at 60 °C (······) and 95 °C (----), and the anhydrous product obtained by heating *cis*-$[Ni(H_2O)_2(NN\text{-dmen})_2]I_2$ at 90 °C (— - —).

may proceed as follows: *trans*-diaqua→*cis*-halogenoaqua→*cis*-dihalogeno species.[14]

The blue iodide isolated as a *cis*-diaqua complex changes to orange species after thermal deaquation. The orange product obtained at 90 °C is diamagnetic and gives a broad band at ca. 20000 $cm^{-1}$ in its spectrum (Fig. 4) assignable to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition of a square planar structure.[15]

In the *NN*-deen complexes, the chloride changed to *cis*-dichloro complex at 100 °C (Table 1) with no formation of chloroaqua species. The bromide became diamagnetic square planar upon dehydration, and the iodide was anhydrous square planar even at room temperature.

**Thermal Reactions of Complex Nitrates.** The complex nitrate with *NN'*-deen undergoes dehydration in one-step. As seen from Table 1, the anhydrous product exhibits two bands at 10100 $cm^{-1}$ and 17000 $cm^{-1}$, indicating that trans-to-cis configurational change takes place simultaneously with deaquation-anation. The coordination mode of nitrate ion was also determined IR spectrophotometrically. It is well-known that, in general, a $NO_3^-$ ion in a metal complex gives rise to a weak combination band in the range of 1700—1800 $cm^{-1}$.[10,15] In the present case, the diaqua complex shows a single peak at 1748 $cm^{-1}$ assignable to the free $NO_3^-$ ions. This peak splits into three peaks at 1718, 1750, and 1767 $cm^{-1}$ in the spectrum at 100 °C. The peak at 1750 $cm^{-1}$ indicates that a part of the $NO_3^-$ ions remains uncoordinated, while the large separation (49 $cm^{-1}$) between the other two peaks indicates that the coordinated $NO_3^-$ ion functions as a bidentate ligand. This reaction can thus be understood as shown below:

$$trans\text{-}[Ni(H_2O)_2(NN'\text{-deen})_2](NO_3)_2 \longrightarrow cis\text{-}[Ni(NO_3)(NN'\text{-deen})_2](NO_3)$$

The TG-DTA curve for *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2](NO_3)_2 \cdot 2H_2O$ (Fig. 2) shows that the complex gives a small but clear exothermic peak at 118 °C with no mass loss after dehydration. The complex changed in color from blue-violet to violet before and after the peak. The enthalpy change of the reaction was estimated to be −6.4 kJ $mol^{-1}$ by means of DSC measurement.[17] The spectral differences between the blue-violet and violet products (Table 1) indicate that this exothermic peak is associated with the cis-to-trans isomerization. The IR band at 1757 $cm^{-1}$ assignable to the free $NO_3^-$ ions of the diaqua complex splits into three peaks at 1718, 1747, and 1767 $cm^{-1}$ in the spectrum at 60 °C (just after dehydration): the peak at 1747 $cm^{-1}$ is due to the free $NO_3^-$ ions, while the other two peaks with a separation of 49 $cm^{-1}$ show the presence of bidentate $NO_3^-$ ions. On the other hand, the spectrum at 130 °C (after the exothermic DTA peak) is split into two peaks with a small separation (16 $cm^{-1}$), showing that the two $NO_3^-$ ions are coordinated as monodentate ligands. These results are consistent with the configurational assignments from the electronic spectra. This reaction can thus be described as follows: *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2](NO_3)_2 \cdot 2H_2O$ first undergoes dehydration-anation accompanied by a trans-to-cis configurational change, yielding *cis*-$[Ni(NO_3)(NN'\text{-dmen})_2](NO_3)$, which then isomerizes to *trans*-$[Ni(NO_3)_2(NN'\text{-dmen})_2]$ at 118 °C. On the other hand, the *NN*-dmen complex shows a simple deaquation-anation, retaining the original trans configuration (Table 1 ).[12]

The corresponding ethylenediamine (en) complex, *trans*-$[Ni(H_2O)_2(en)_2](NO_3)_2$, was also studied, the results of which are contained in Tables 1 and 2. This complex first transformed into the violet *trans*-dinitrato complex upon deaquation-anation. Then the *trans*-dinitrato complex isomerized to blue-violet *cis*-mononitrato species at 170 °C, which is in contrast to the above case of the *NN'*-dmen complex. This isomerization was endothermic and reversible.

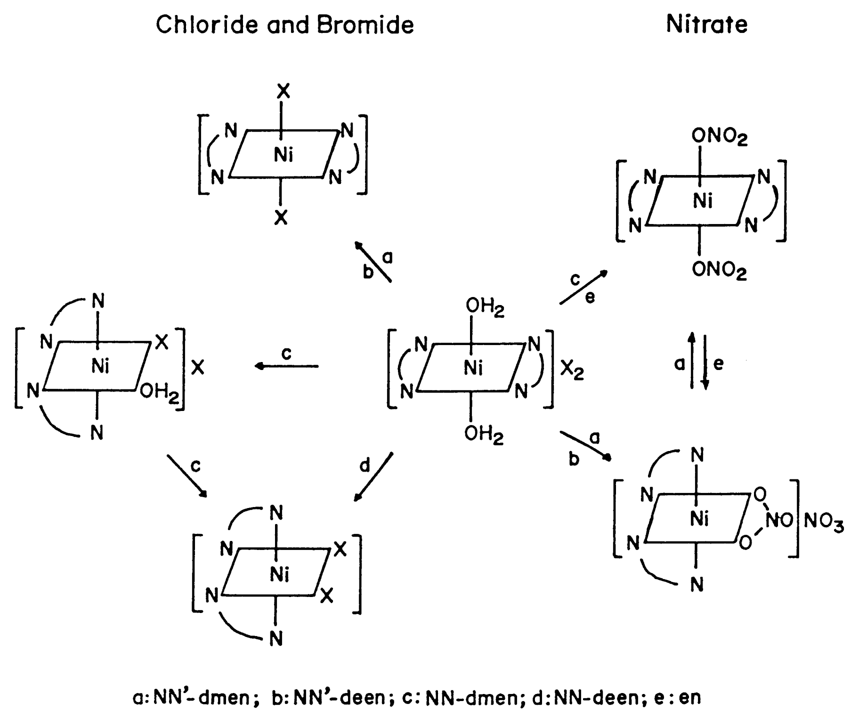
## Discussion

Scheme 1 summarizes the thermal reaction pathways of the complex chlorides, bromides, and nitrates clarified in this work. The thermal behaviors of the complex nitrates are quite different from those of the halides, and the reactions of the complexes with the symmetric diamines are different from those of the asymmetric ones. It is thus clear that the preferred geometry of a complex depends on the combination of diamine and anion, and either trans or cis configuration is strongly stabilized for a particular combination of ligands.[18]

In the case of halides, the *NN'*-dmen and *NN'*-deen complexes undergo dehydration-anation, during which their trans configurations are retained; the anation takes place at the axial positions which are occupied by the water molecules before heating. On the other hand, the stable halogenoaqua species can be isolated for the complex halides of *NN*-dmen, since two moles of coordinated waters are liberated one by one in two separate steps. Another significant feature of the complexes with asymmetric diamines is that cis configuration is favored in both halogenoaqua and dihalogeno complexes.

Such peculiar reactions of the asymmetric diamine complexes must be associated with the structures of starting diaqua complexes. According to the X-ray structural study[13] on *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$ and *trans*-$[Ni(H_2O)_2(NN\text{-deen})_2]Cl_2$, both complexes take tetragonally distorted octahedrons with four in-plane neighbors $(N(H_2)N(H_2)OO)$ and two remote axial ones $(N(R_2)N(R_2))$:[19] i.e., the two alkylated nitrogen atoms occupy axial sites apart from each other to minimize their mutual steric hindrance and the distances of $Ni-N(R)_2$ bonds are remarkably longer than the other. These structural results are obviously different from those of the symmetric diamine complexes with the stronger Ni–NH(R) bonds.[20,21] Thus, it appears reasonable to assume that, in the case of the complexes with asymmetric diamines, a process of the $Ni-NR_2$ bond rupture is involved in the mechanism of thermal deaquation-anation.

In the case of the nitrates, interesting thermal




Scheme 1.

cis→trans and trans→cis isomerization were observed in the anhydrous complexes with *NN'*-dmen and en, respectively. On the other hand, only the *NN*-dmen complex kept the original geometry upon dehydration and showed no isomerization after dehydration.

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