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論　文

# Thermal Properties of the Complex of bis-iso-butanediamine Nickel(II) Chloride, $[Ni(i\text{-}bn)_2]Cl_2$

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$[Ni(i\text{-}bn)_2]Cl_2$, was isomerized thermally from a square planar structure to a *cis* octahedral one by the coordination of counter ion, $Cl^-$, at around 180 − 190℃, where i-bn is iso-butanediamine (2-methyl-1,2-propanediamine). The isomerization was accompanied by thermochromism from yellow to light blue. When the yellow complex was permitted to stand for a few hours in air, it was converted to *trans*-$[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2 \cdot 2H_2O$ and the color changed from yellow to violet.

The dehydration of *trans*-$[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2 \cdot 2H_2O$ took place simultaneously with the anation of $Cl^-$ ions at around 50℃. On the dehydration-anation, the structure of the complex changed from a *trans* octahedral to a *cis* octahedral without forming the square planar structure, and the color changed from violet to light blue.

The isomerization of $[Ni(i\text{-}bn)_2]Cl_2$ and the dehydration − anation of *trans*-$[Ni(H_2O)_2 \cdot (i\text{-}bn)_2]Cl_2 \cdot 2H_2O$ were considered to be the Avrami − Erofe'ev type reactions, and the activation energies were evaluated to be 305.7 and 59.2 kJ $mol^{-1}$, respectively.

## 1. Introduction

Ihara *et. al.*[1] have reported that the complex of $[Ni(i\text{-}bn)_2]Cl_2$ is isomerized from a square planar structure (Sp) to an octahedral structure (Oh) by the coordination of chloride ions, $Cl^-$, at around 180℃, where i-bn is iso-butanediamine (2-methyl-1,2-propanediamine), $NH_2CH_2C(CH_3)_2NH_2$. Then the color of the complex changes from yellow to light blue.

$$\begin{array}{lcll} [Ni(i\text{-}bn)_2]Cl_2 & \rightarrow & [NiCl_2(i\text{-}bn)_2] & \text{(a)} \\ \text{Sp, yellow} & & \text{Oh, light blue} & \end{array}$$

When the yellow complex was permitted to stand for a few hours in air, the color of the complex changed to violet. However, Ihara *et. al.* did not mention about the violet complex. Heating the violet complex to at around 50℃, the complex was converted directly to the light blue one, *cis*-$[NiCl_2(i\text{-}bn)_2]$, without through the yellow complex, $[Ni(i\text{-}bn)_2]Cl_2$.

In the present paper, the structural changes and the kinetics of these complexes were studied by means of thermal analyses of thermogravimetry (TG), differential thermal analysis (DTA) and diffrential scanning calorimetry (DSC), and by the visible electronic spectra of these solid complexes.

## 2. Experimental

### 2.1 Preparation of Compound

iso-Butanediamine (2-methyl-1,2-propanediamine) was commercial product of reagent grade, and was used

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without further purification. The complex, $[Ni(i\text{-}bn)_2]\cdot Cl_2$, was prepared according to the literature,[1-3] and identified by elemental analysis, and spectral and magnetic measurements.[1]

### 2.2 Apparatus

TG and DTA were performed with a Rigaku Thermoflex TG-DTA MJ800PF2. DSC curves were obtained by a Shinku-Riko DSC-1500 M5/L. The output voltages of the DSC were amplified by a Unipulse U350A and the data were acquired on a microcomputer, Epson QC10-II, via an AD converter, Thinky SC-51.[4-6] The DSC measurements were performed at heating rates of 2.3, 3.4, 4.6 and 6.9 K $min^{-1}$ with using $\alpha$-alumina as a reference material. The energy output of the DSC was calibrated from the heats of transition of potassium nitrate ($T_{trs}=400.9$ K, $\Delta H_{trs}=5.4$ kJ$mol^{-1}$) and of fusion of indium (99.999%) ($T_{fus}=430$ K, $\Delta H_{fus}=3.3$ kJ $mol^{-1}$).[7]

Visible electronic spectra of the solid phases were measured with a Hitachi U-3200 spectrophotometer equipped with a head-on photomultiplier. Spectra at elevated temperatures were obtained using a heating block.[4,5]

### 2.3 Kinetic Analysis

The kinetics of the thermal reaction of the solid complex was studied on the basis of the DSC measurements.[4,5] The rate of the thermal reaction is generally expressed by

$$d\alpha/dt = k\ F(\alpha) \qquad (1)$$

where $\alpha$ is the fraction of reaction after time $t$, $F(\alpha)$ is a function depending on the reaction mechanism,[8-11] and $k$ is a rate constant which is related to absolute temperature, $T$, according to the Arrhenius equation

$$k = A\ \exp(-E/RT) \qquad (2)$$

where $A$, $E$ and $R$ are the pre-exponential factor, the activation energy and the gas constant, respectively. Substituting eq.(2) and a linear heating rate, $\beta = dT/dt$, into eq.(1),

$$[(d\alpha/dT)\beta] = A\ \exp(-E/RT)\ \ F(\alpha) \qquad (3)$$

and the logarithmic form of eq.(3)

$$\ln\ [(d\alpha/dT)\beta] - \ln\ F(\alpha)\ = \ln\ A - E/RT \qquad (4)$$

The rate of reaction $[(d\alpha/dT)\beta]$ was directly obtained from the DSC measurements, and the suitable function $F(\alpha)$ was determined from the linearity of the plots of the left-hand side against $1/T$ in accordance with eq.(4) (Achar's plot).[8] Activation energy, $E$, was determined from the slope. The $E$ obtained was checked by the modified Friedman method described previously.[4,5,12] In order to determine $A$, the experimental values of $[(d\alpha/dT)\beta]$, $E$ and $F(\alpha)$ were introduced into eq.(4).

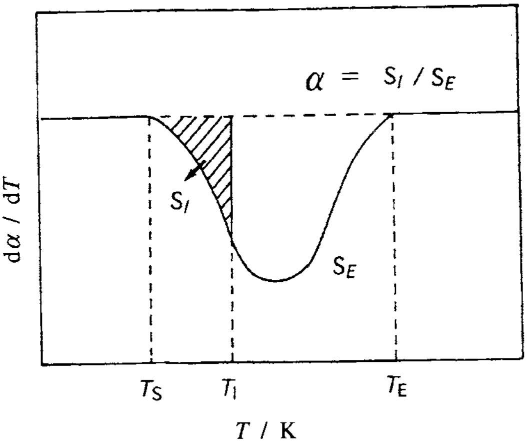

**Fig.1** Determination of reaction fraction, $\alpha$ obtained from DSC curve: $S_E$ is total area of this peak; $S_I$ is area evolved up to temperature, $T_I$; $T_S$ and $T_E$ are the temperatures at which reaction starts and ends, respectively.

The reaction fraction, $\alpha$ at the temperature $T_I$ was derived from the ratio of the area, $S_I$, corresponding to the heat evolved up to $T_I$ to the total integrated area of the heat of reaction, $S_E$, as shown in **Fig.1**.[4]

## 3. Results and Discussion

The TG-DTA curves are given in **Fig.2**. Solid curves correspond to the yellow complex, $[Ni(i\text{-}bn)_2]Cl_2$, and the endothermic peak observed at around 180℃ is attributable to the isomerization from the Sp to the Oh by the coordination of Cl ions.[1] The dotted TG-DTA curves belong to the violet complex obtained from permitting the complex, $[Ni(i\text{-}bn)_2]Cl_2$, to stand for a few hours in air. An endothermic peak observed at 50℃ was accompanied by weight loss for 4 moles of water. Before and after the endothermic peak, the color of the complex changed from violet to light blue. From these

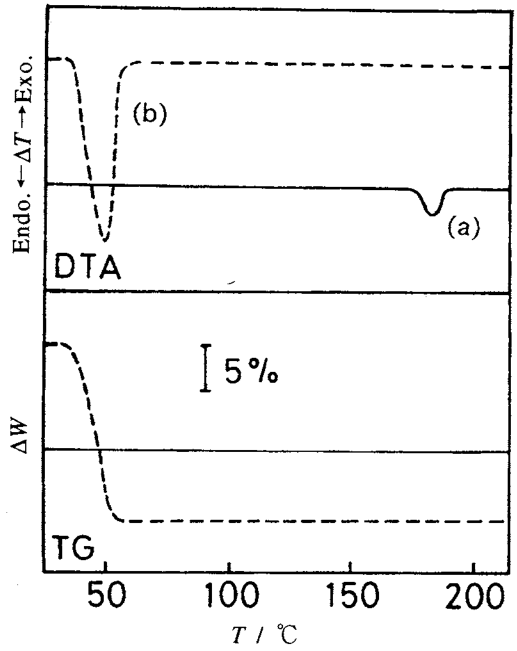

**Fig.2** TG-DTA curves (heating rate; 4 K $min^{-1}$) of the complex, $[Ni(i\text{-}bn)_2]Cl_2$ (____) and the violet complex obtained from permitting the complex, $[Ni(i\text{-}bn)_2]Cl_2$ to stand for a few hours in air (_ _ _).

findings the violet complex seemed to be a diaqua complex which has a trans Oh structure such as the complex with dl-bn (dl-2,3-butane-diamine),[5] and the trans Oh structure would be transformed to the cis Oh structure as follows,

$$\underset{\text{Oh, violet}}{trans\text{-}Ni(H_2O)_2(i\text{-}bn)_2]Cl_2\cdot 2H_2O} \rightarrow \underset{\text{Oh', light blue}}{cis\text{-}NiCl_2(i\text{-}bn)_2]} + 4H \qquad (b)$$

On the transformation (b), the anation of $Cl^-$ ions seemed to proceed simultaneously with the dehydration. **Figure 3** shows schematic expression of the structural change expected from the isomerization (a) and the dehydration – anation (b).

The structural distinction between *cis* and *trans* isomers of the bis(diamine)nickel(II) complexes has already been established by means of the electronic spectroscopy.[2,13-16] The energy levels derived from *F* and *P* terms of a $d^8$ system of $Ni^{2+}$ in ligand fields of different symmetries such as Oh, $D_{4h}$ and $C_{2v}$ are given in **Fig.4** together with the rough sketches of the typical electronic spectra of *trans*- and *cis*-$[NiX_2\cdot(diamine)_2]$. **Table 1** summarized the spectral data of the violet complex and light blue complexes obtained by heating the violet and yellow ones (**Figs.3 and 4**). The band maxima of the light blue complex obtained after the dehydration – anation well agreed with those of the dimer of *cis*-$[NiCl_2(i\text{-}bn)_2]$, so the light blue complex is assigned to *cis*-$[NiCl_2(i\text{-}bn)_2]$ which would formulate the dimer.[3] The band maxima of light blue

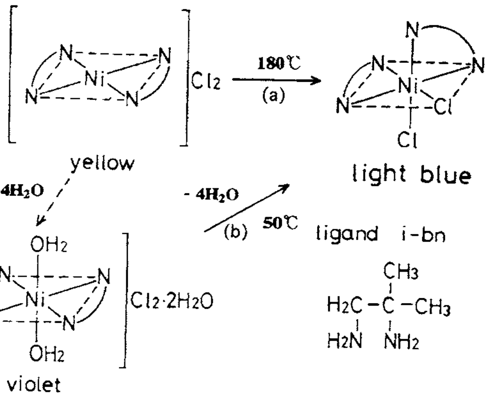

**Fig.3** Schematic expression of isomerization, (a) and dehydration-anation, (b) of the complexes with i-bn.

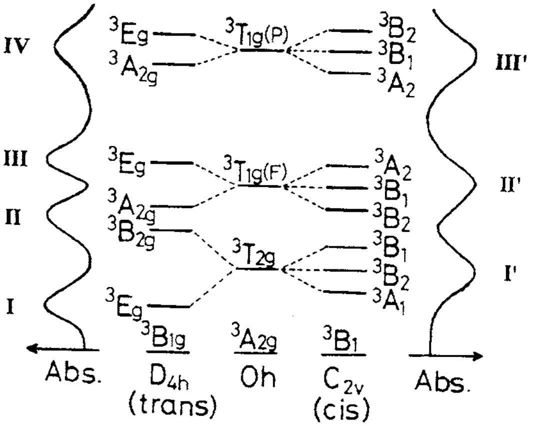

**Fig.4** Energy level diagrams of a $d^8$ system in ligand fields of different symmetries. Sketches of the absorption spectra of the *cis* and *trans* isomers of $[NiX_2(diamine)_2]$ are given. I, II, III, IV, I', II' and III' mean the absorption band maximum of the complexes.

**Table 1** Electronic Spectral Data.*

| | | Absouption Band Maxima $\nu$ /10$^3$ cm$^{-1}$<br>I** | II | III | IV |
|---|---|---|---|---|---|
| $[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2 \cdot 2H_2O$ | Ihara 1) | 9.0 | 13.5 | 18.0 | 28.5 |
| | Ferago 3) | 9.7 | 13.6 | 17.8 | 28.4 |
| violet complex | | — | 13.5 | 17.9 | 28.9 |
| | | I'** | II' | III' | |
| $[NiCl_2(i\text{-}bn)_2]$ | Ihara 1) | 10.4 | 17.2 | 27.2 | |
| | Ferago 3) | 9.9 | 17.9 | 27.3 | |
| light blue complex obtained by heating yellow complex up to 180℃ | | — | 17.2 | 27.1 | |
| light blue complex obtained by heating violet complex up to 50℃ | | | — | 17.2 | 27.4 |

* Absorption band maxima,I, II, III, IV, I', II" and III' are corresponding to those shown in Fig.4.

** The band could not be measured with a Hitachi U-3200 spectrometer.

**Table 2** $F(\alpha)$, activation energy ($E$), pre-exponential factor ($A$) and enthalpy change ($\Delta H$) for the isomerization (a) and dehydration-anation (b).

| Reaction | $F(\alpha)$ | $E$ / kJ mol$^{-1}$ | log ($A$ / s$^{-1}$ ) | $\Delta H$ / kJ mol$^{-1}$ |
|---|---|---|---|---|
| (a) | A1.4 * | 305.7 ±9.05 | 33.3 | 12.1 ±0.94 |
| (b) | A2 * | 59.2 ±4.86 | 7.6 | 199.1 ±4.9 |

$A_n{*} = (1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$

complex obtained by heating the yellow complex up to 180℃ are well corresponding with those of the complex obtained by heating the violet complex, indicating that both the light blue complexes are the same one. On the other hand, the band maxima of the violet complex well agreed with those of *trans*-$[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2 \cdot 2H_2O$,[1,3] therefore, the violet complex is assigned to *trans*-$[Ni(H_2O)_2 \cdot (i\text{-}bn)_2]Cl_2 \cdot 2H_2O$.

These results suggest that the dehydration and anation of $Cl^-$ would take place simultaneously in the violet complex, *trans*-$Ni(H_2O)_2(i\text{-}bn)_2]Cl_2 \cdot 2H_2O$, according to eq.(b).

**Figure 5** shows the plots of activation energies, $E$ vs. $\alpha$ for the isomerization (a) and the dehydration – anation (b). The value of $E$ for the reaction (b) was fairly lower than that for the reaction (a). This fact is consistent with that the dehydration – anation (b) takes place at fairly lower temperature than that of the iso-

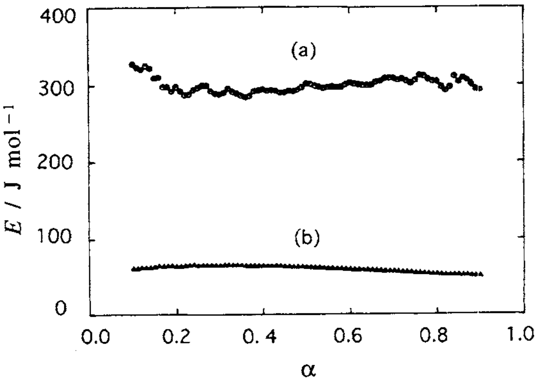

**Fig.5** Relationship between $E$ and $\alpha$ for the isomerization (a) and the dehydration-anation (b).

merization (a). The lower $E$ value for (b) can be ascribable as follows. In the isomerization (a), the process involving anation of $Cl^-$ may consist of three steps; at first the counter ion leaves from the lattice site, then migrates to the complex cation, and finally the chelate ring is twisted to form a *cis* configuration. On the other hand, the dehydration − anation (b) is more complicated than that of (a). In the process (b), the lattice expansion may be caused by the water molecules dehydrated,[17] and the lattice expansion would be expected to facilitate the twisting of the chelate ring to *cis* structure. Therefore, it is reasonable that the value of $E$ for (b) is lower than that for (a).

The value of enthalpy changes ($\Delta H$) and the mechanism functions, $F(\alpha)$ of these thermal reactions are summarized in **Table 2**. The large value of $\Delta H$ for (b) seems to reflect the complicated dehydration-anation steps. The reactions (a) and (b) were seemed to be described by model functions of Avrami–Erofe'ev type, $A_{1.4}$ and $A_2$, respectively. The $A_n$ model, where $A_n = (1-\alpha)\ [-\ln(1-\alpha)]^{(n-1)/n}$ and $1 < n \leqq 2$, is the kinetic expression concerned with random nucleation and nuclei growth processes.[9] Hulbert[9] has pointed out the relationship between the nuclei growth and the diffusion processes of the migrating species as follows. When the nucleation rate is assumed to be constant, the nuclei grow two-dimensionally and the growth is controlled by the diffusion of the migrating species, then the $A_n$ expression can be derived. Although the rates of nucleation for both the reactions (a) and (b) are different each other, their nuclei growth seems to be controlled by the two-dimensional diffusion of $Cl^-$ or $H_2O$, respectively.[8]

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## 要　旨

平面正方型錯体, $[Ni(i\text{-}bn)_2]Cl_2$（i-bn：イソブタンジアミン）は180～190℃に熱すると，塩化物イオンの配位によって異性化して，八面体型構造に変化し，錯体の色は黄色からライトブルーに変化することが知られている。この黄色の錯体は，空気中に数時間放置すると，*trans*-$[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2\cdot 2H_2O$に変化し，その色は紫色に変化することがわかった。この錯体*trans*-$[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2\cdot 2H_2O$を50℃に熱すると，脱水と塩化物イオンのアネーションが同時に起こり，錯体は平面正方型錯体を経ずに，八面体型の*cis*-$[NiCl_2(i\text{-}bn)_2]Cl_2$に変化し，錯体の色は紫からライトブルーに変化することがわかった。これらの熱異性化反応および脱水－塩化物イオンのアネーション反応は，Avrami-Erofe'ev型の反応であって，それらの活性化エネルギーはそれぞれ305.7および59.2 kJ $mol^{-1}$であった。