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THERMAL SQUARE PLANAR-TO-OCTAHEDRAL TRANSFORMATION OF NICKEL(II) COMPLEXES CONTAINING BUTANEDIAMINES IN A SOLID PHASE

Y. IHARA, T. KAMISHIMA

Chemistry Laboratory, Faculty of Education, Kanazawa University, Kanazawa (Japan)

R. TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa (Japan)

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ABSTRACT

Thermal reactions of the nickel(II) complexes, $[Ni(m\text{-bn or i-bn})_2]X_2$ and $[Ni(H_2O)_2(dl\text{-bn})_2]X_2 \cdot n\ H_2O$, where m-bn, i-bn, and dl-bn are meso-2,3-butanediamine, 2-methyl-1,2-propanediamine, and dl-2,3-butanediamine, respectively, X is Cl^-, Br^-, I^-, NO_3^-, or ClO_4^-, and *n* is 2 for bromide, and 0 for the others, were investigated in a solid phase before and after heating using thermal analyses (TG and DSC) and spectral and magnetic measurements. In the case of the chloride and bromide, the square planar bis(dl-bn) complexes obtained by dehydration of the respective diaqua complexes were transformed to the octahedral diacido bis(dl-bn) complexes upon further heating. The same structural transformation was observed in the thermal reactions of $[Ni(m\text{-bn})_2](NO_3)_2$ and $[Ni(i\text{-bn})_2]Cl_2$. It was summarily recognized that such square planar-to-octahedral transformation was favored in the order dl-bn > i-bn > m-bn complexes in the respective halides, and it was a reversible thermochromism from yellow to blue. The changes in enthalpy of the reactions were endothermic and fell in the range of about 10–20 kJ $mole^{-1}$. The possibility of such configurational change seems to be dependent mainly upon the ionic radius of the X anion, the orientation of two C-substituted methyl groups on butanediamines in the formation of the complexes, and the thermal stability of the complexes themselves.

INTRODUCTION

It is well known that the nickel(II) ion forms complexes of various structures, e.g. octahedral, tetrahedral, and square planar, depending upon the ligands, mutual transformations often occurring amongst them [1]. In 1939, Lifschitz et al. [2] observed that the $[Ni(\text{stien or phenen})_2]X_2 \cdot n\ H_2O$ complexes (stien: 1,2-diphenyl-1,2-ethanediamine; phenen: 1-phenyl-1,2-ethanediamine; X: Cl^-, $ClCH_2COO^-$, $HCOO^-$, and 1/2 SO_4^{2-}; *n*: 0–4) easily undergo mutual transformation (yellow diamagnetic ↔ blue paramagnetic species), with a slight variation depending upon X and the hydra-

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tion state. Since then, such configurational change or equilibration between any two of the three types has often been found in aqueous and some organic solvents [3,4]. However, few studies in the solid phase are known.

Recent studies of nickel(II) complexes on thermal analyses in the solid phase indicated that there are two types of reaction involving the configurational change described above. One type is the reaction represented by the thermal behavior of octahedral diaquabis(*N*,*N*-diethylethylenediamine) complexes, which lose two coordinated water molecules to produce the octahedral diacido complex, accompanied by anation of counter anions for the chloride, and the square planar structure only by dehydration for bromide upon heating [5]. These reactions are also observed in the complexes containing other ethylenediamines [6,7]. The occurrence of either deaquation–anation or deaquation is attributable to a selection of ethylenediamines and counter anions. In tris(diamine) complexes, the liberation of 1 mole of diamine under thermal decomposition produces the same change owing to deamination–anation or deamination [6].

Another type is a structural transformation from square planar to tetrahedral or octahedral without the liberation of any ligands. The complexes with *N*-methylsalicylideneamines and benzimidazoles present examples of the change to tetrahedral [8,9] and octahedral structures [10,11], respectively.

On the other hand, it is already known that both diaquabis(dl-bn) nickel(II) chloride and bromide evolve 2 moles of coordinated water to be converted into the square planar form upon heating, where dl-bn is dl-2,3-butanediamine [6]. The literature predicts, moreover, that continued heating after dehydration causes them to undergo a second reaction of structural transformation from square planar to octahedral by anation.

The aim of the present study was to confirm the above transformation of dl-bn complexes clearly by means of DSC, to follow the possibility of similar reactions of other salts of dl-bn complexes and the complexes containing m-bn or i-bn, where m-bn and i-bn are meso-2,3-butanediamine and 2-methyl-1,2-propanediamine, respectively, and to consider the effect of choice of diamines and counter ions upon the transformation of complexes by comparison of their reactivities.

EXPERIMENTAL

Preparation

The ligands, dl-bn and m-bn, and their complexes, $[Ni(H_2O)_2(dl\text{-}bn)_2]X_2 \cdot n\ H_2O$ and $[Ni(m\text{-}bn)_2]X_2$, were obtained using the methods described in refs. 12 and 6, respectively. The i-bn were of commercial reagent grade and were used without further purification. Preparation of the complexes, $[Ni(i\text{-}bn)_2]X_2$, was carried out according to the literature [13]. Five univalent anions, Cl^-, Br^-, I^-, NO_3^-, and ClO_4^-, were selected as X counter ions. Their chemical formulas were determined by elemental analyses and by spectral and magnetic measurements.

Thermal analyses

Simultaneous TG and DSC measurements were carried out with a Rigaku Denki standard TG–DSC apparatus. Each run was under a constant flow of nitrogen at a heating rate of 1.25°C min^{-1}; about 15–30 mg of sample was used. The heated products after transformation were obtained by isothermal heating at the temperatures of the respective DSC peaks, using an electric furnace in static air.

Spectral measurements

The electronic spectra in the solid state were measured by a diffuse reflectance method with a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment (Type R-3). The far-IR spectra were measured by the Nujol method with a JASCO DS-701G diffraction grating IR spectrophotometer.

Magnetic measurements

The effective magnetic moments were evaluated from the magnetic susceptibilities measured by the Gouy method at room temperature. $Hg[Co(NCS)_4]$ was employed as reference material. The susceptibilities were corrected using Pascal's constants for each element or atomic group contained in the complex.

RESULTS AND DISCUSSION

Complexes with m-bn or i-bn

In the ten complexes prepared, the specimens showing obvious changes in the DSC curves before their decomposition points were nitrate and perchlorate in the m-bn complexes and chloride and nitrate in the i-bn complexes. The results are shown in Fig. 1, in which the TG curves are neglected, since no weight loss is observed until their decomposition temperatures begin at 260, 235 < , 208, and 233°C for nitrate and perchlorate of m-bn and chloride and nitrate of i-bn complexes, respectively. From Fig. 1, an endothermic reaction is found to occur at near 195, 198, 172, and 175°C for m-bn nitrate, perchlorate, i-bn chloride, and nitrate, respectively. In addition, a distinct thermochromism from yellow to bluish violet for m-bn nitrate and

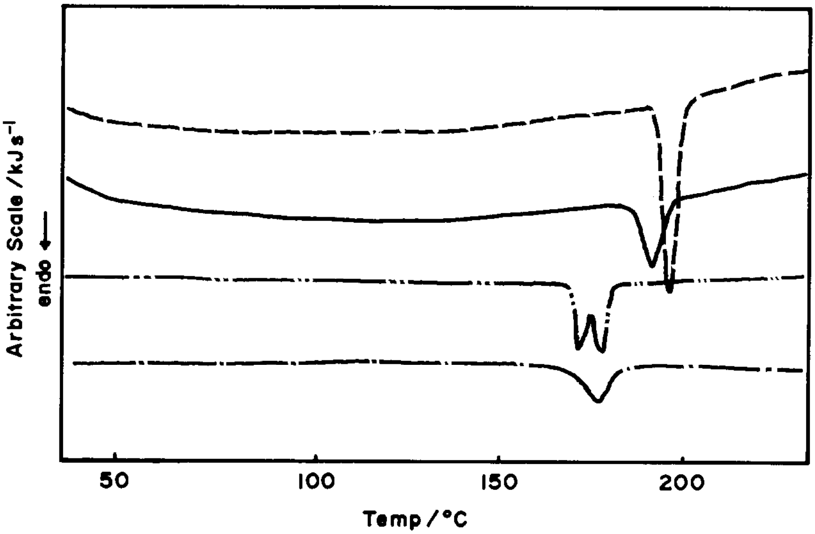

Fig. 1. DSC curves of $[Ni(m\text{-}bn)_2](NO_3)_2$ (————), $[Ni(m\text{-}bn)_2](ClO_4)_2$ (- - - - - -), $[Ni(i\text{-}bn)_2]Cl_2$ (– - - - –), and $[Ni(i\text{-}bn)_2](NO_3)_2$ (– - - –).

to blue for i-bn chloride is observed upon heating at the temperatures where the endothermic peaks appear. The reverse color change proceeds on cooling at room temperature, slow enough to take several days to return completely to the original yellow color.

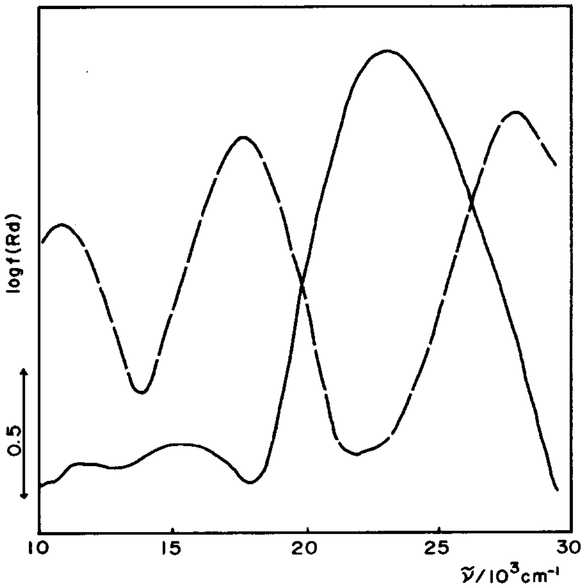

Fig. 2. Electronic spectra of $[Ni(m\text{-}bn)_2](NO_3)_2$ before heating (————) and after heating (- - - - - -).

Although the other complexes, m-bn perchlorate and i-bn nitrate, show a similar reversible color change between yellow and orange at the DSC peaks, it is likely that the change is not so drastic as to suggest a distinct structural transformation.

The electronic spectrum of $[Ni(m\text{-}bn)_2](NO_3)_2$ is given in Fig. 2, together with one obtained by heating it to the temperature where an endothermic reaction has been completed on the basis of the DSC curve. The original complex has one relatively strong absorption band near 23×10^3 cm^{-1} due to a square planar structure of nickel(II) complexes, but the heated product gives a spectral pattern having three absorption bands characteristic of the octahedral structure.

Similar results can also be observed in i-bn chloride, as given in Fig. 3 which includes the spectra of the complexes before and after heating, together with that of the octahedral diaqua complex, $[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2$, prepared from aqueous solution. As shown in Fig. 3, the spectral pattern of the blue heated product is found to be nearly identical to that of the diaqua complex, the shifts of wave number showing absorption maxima due to the difference in coordinated Cl^- and H_2O being observed between both octahedral complexes.

The analytical data, the wave numbers giving absorption maxima, and the magnetic moments of the original complexes and heated products concerned are collected in Tables 1 and 2, including those of dl-bn complexes described later. In m-bn nitrate and i-bn chloride, the change from diamagnetic to paramagnetic of about 3.0 B.M. upon heating suggests a structural transformation from square planar to octahedral.

Figure 4 compares the far-IR spectrum of the m-bn nitrate with that of

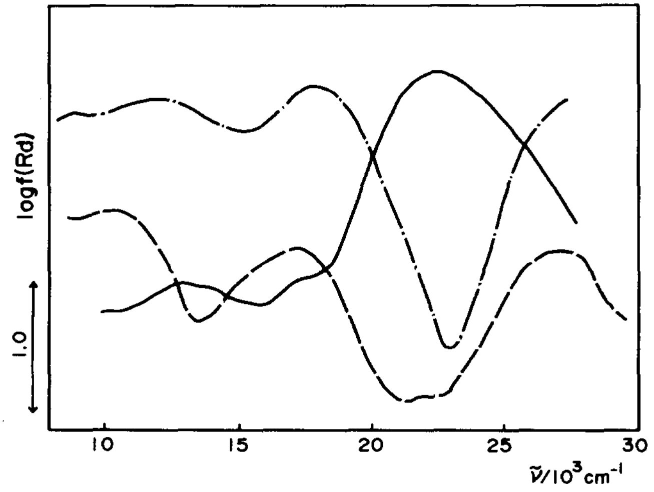

Fig. 3. Electronic spectra of $[Ni(i\text{-}bn)_2]Cl_2$ before heating (————) and after heating (- - - - -), and that of $[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2$ (– - - - –).

TABLE 1

Analytical data, electronic spectral data, and magnetic moments of the original complexes

Complexes	Color	Analytical data [a]			Absorption maxima	$\mu_{eff.}$(B.M.)
		C(%)	H(%)	N(%)	$\tilde{\nu}(10^3\ cm^{-1})$	
$[Ni(m\text{-}bn)_2](NO_3)_2$	Yellow	26.46 (26.76)	6.82 (6.74)	23.21(23.41)	22.9	Diamagnetic
$[Ni(i\text{-}bn)_2]Cl_2$	Yellow	31.37 (31.41)	8.11 (7.91)	18.49 (18.31)	22.5	Diamagnetic
$[Ni(H_2O)_2(dl\text{-}bn)_2]Cl_2$	Violet	27.98 (28.10)	8.32 (8.25)	16.33 (16.38)	12.8 17.9 28.7	3.11
$[Ni(H_2O)_2(dl\text{-}bn)_2]Br_2 \cdot 2\ H_2O$	Reddish violet	20.75 (20.58)	6.60 (6.92)	12.04 (12.00)	13.9 18.2 28.4	3.12
$[Ni(H_2O)_2(dl\text{-}bn)_2]I_2$	Reddish violet	18.31 (18.31)	5.38 (5.38)	10.69 (10.67)	14.3 18.5 28.7	3.13

[a] Calculated values are in parentheses.

TABLE 2

Analytical data, electronic spectral data, and magnetic moments of the heated products

Products	Color	Analytical data [a]			Absorption maxima	$\mu_{eff.}$(B.M.)
		C(%)	H(%)	N(%)	$\tilde{\nu}(10^3\ cm^{-1})$	
$[Ni(NO_3)_2(m\text{-}bn)_2]$	Bluish violet	26.67 (26.76)	6.83 (6.74)	23.43 (23.41)	10.9 17.7 28.0	3.13
$[NiCl_2(i\text{-}bn)_2] \cdot H_2O$	Blue	31.33 (31.41)	8.16 (7.91)	18.27 (18.31)	10.4 17.2 27.2	2.90
$[Ni(dl\text{-}bn)_2]Cl_2$ [b]	Yellow	31.40 (31.41)	8.31 (7.91)	18.25 (18.31)	22.9	Diamagnetic
$[NiCl_2(dl\text{-}bn)_2] \cdot H_2O$	Violet	29.81 (29.66)	8.20 (8.11)	17.44 (17.30)	14.3 18.2 28.1	2.94
$[Ni(dl\text{-}bn)_2]Br_2 \cdot H_2O$ [b]	Yellow	23.68 (23.71)	6.33 (6.36)	13.65 (13.57)	22.9	Diamagnetic
$[NiBr_2(dl\text{-}bn)_2]$	Bluish violet	24.47 (24.34)	6.31 (6.13)	14.52 (14.19)	14.3 17.9 29.4	3.00
$Ni(dl\text{-}bn)_2I_2$	Pale brown	18.67 (18.96)	5.02 (5.18)	11.23 (11.06)	10.9 19.2 21.7	2.25

[a] Calculated values are in parentheses.

[b] Products after dehydration.

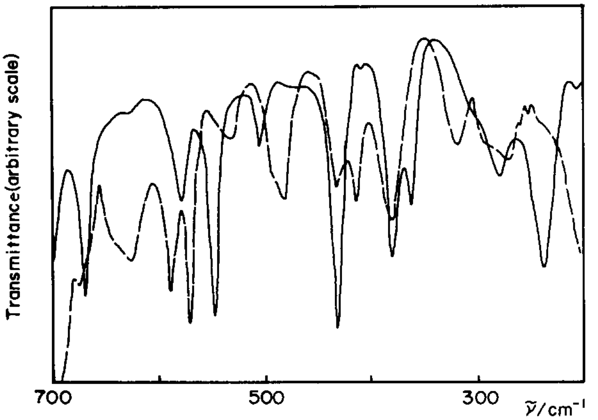

Fig. 4. Far-IR spectra of $[Ni(m\text{-}bn)_2](NO_3)_2$ before heating (————) and after heating (------).

the heated product. A pronounced difference between the two spectra is that the absorption band of 313 cm^{-1} reappears after heating. Ferraro and Walker [14] pointed out that anhydrous metal nitrates, $Cu(NO_3)_2$ and $Co(NO_3)_2$, exhibit a peak in the range 250–350 cm^{-1} assigned to metal–oxygen vibration due to coordination of the nitrate ion to the central metal; so, the new peak of 313 cm^{-1} appearing in the heated product can be ascribed to the $Ni\text{–}O(NO_3)$ stretching vibration. The nitrate ion situated in the outer sphere before heating, therefore, approaches the central metal to form the coordinated bond in the product.

The thermochromism from yellow to blue of $[Ni(i\text{-}bn)_2]Cl_2$ can also be considered to result from the structural transformation from square planar to octahedral structure such as the case of $[Ni(m\text{-}bn)_2](NO_3)_2$, according to the results of measurements of the complex before and after heating described in Tables 1 and 2.

Complexes with dl-bn

Since the preparation of square planar complexes containing dl-bn is difficult, the octahedral diaqua complexes, $[Ni(H_2O)_2(dl\text{-}bn)_2]X_2 \cdot n\ H_2O$, were selected as starting materials. They may easily lose their lattice water and coordinated water to form square planar complexes by standing in a silica gel desiccator for several weeks (except for iodide).

The TG–DSC patterns of five diaqua complexes are given in Fig. 5. Heating of the complexes obviously leads to the generation of square planar complexes due to deaquation at the first step of thermal reaction as shown in Fig. 5 and Tables 1 and 2, except for iodide. The dehydration starts earlier at room temperature and becomes complete at about 100°C.

Both chloride and bromide develop a second endothermic peak, predicting

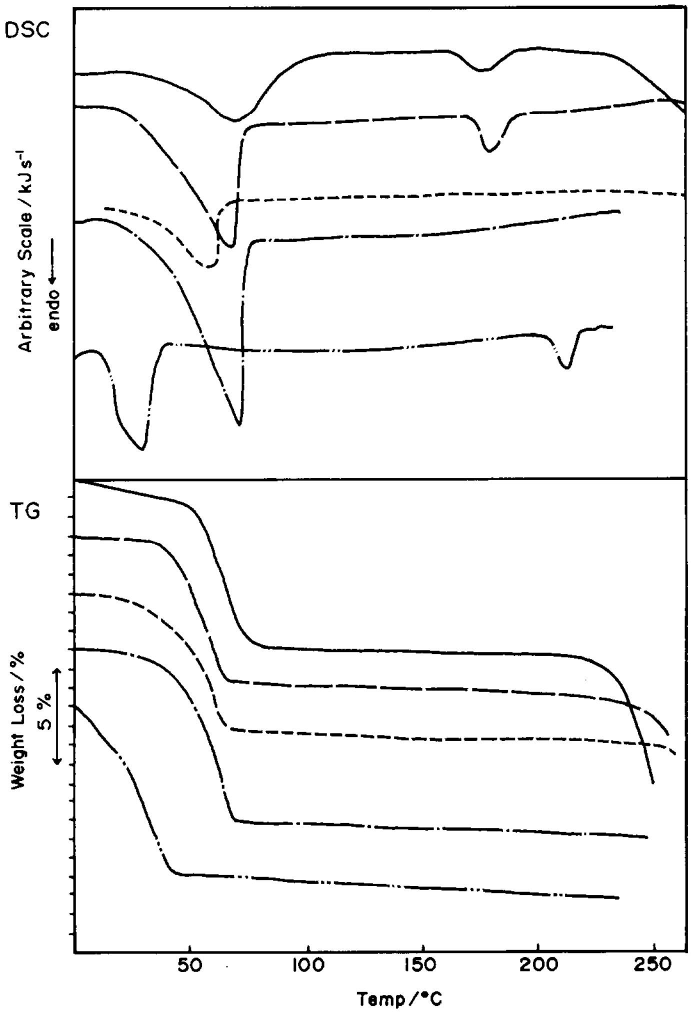

Fig. 5. TG–DSC patterns of $[Ni(H_2O)_2(dl\text{-}bn)_2]X_2$, chloride (————), bromide dihydrate (— — —), iodide (- - - - - -), nitrate (– - – - –), and perchlorate (– - - –).

a transfer reaction after deaquation, where no change is recognized in the TG curves, so retaining a plateau. The color of the complexes then converts to violet and bluish violet from yellow in the chloride and bromide, respectively. The reversible thermochromism examined in both complexes coincides with that in the case of $[Ni(m\text{-}bn)_2](NO_3)_2$ and $[Ni(i\text{-}bn)_2]Cl_2$ described in the preceding section, which is supported by the spectral and magnetic data in Fig. 6 and Tables 1 and 2. It is concluded, therefore, that the stepwise thermochemical change

octahedral(diaqua) → square planar → octahedral(diacido)

occurs in the complexes, as presumed previously in ref. 6. On the other hand,

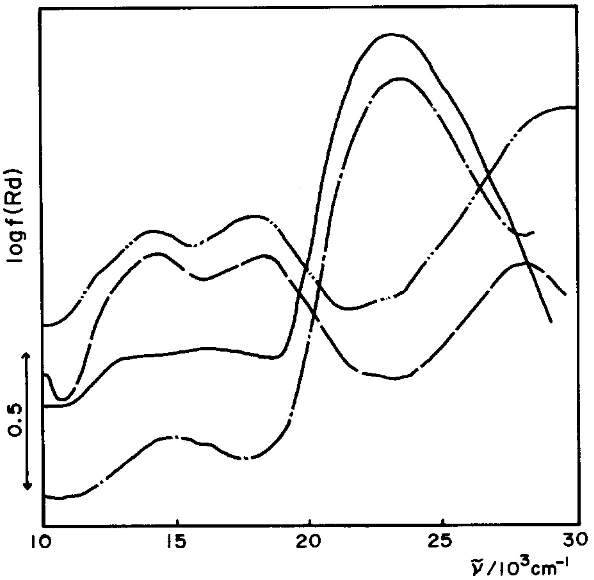

Fig. 6. Electronic spectra of $[Ni(dl\text{-}bn)_2]Cl_2$ before heating (————) and after heating (- - - - - -); and $[Ni(dl\text{-}bn)_2]Br_2$ before heating (– – – – –) and after heating (– - – –).

no such transformation could be found, thereafter, in the corresponding nitrate and perchlorate, having a square planar structure after dehydration, although in the perchlorate the endothermic peak at 195–220°C, indicating the melting, is observed.

The violet species of the iodide, $[Ni(H_2O)_2(dl\text{-}bn)_2]I_2$, turns to pale brown, but to neither yellow nor blue, when dehydrated upon heating, being different from the other salts which produce yellow square planar complexes.

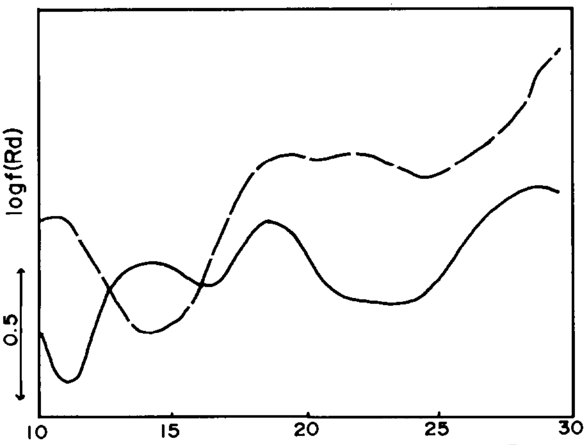

Fig. 7. Electronic spectra of $[Ni(H_2O)_2(dl\text{-}bn)_2]I_2$ before heating (————) and after heating (- - - - - -).

As shown in Tables 1 and 2, the magnetic moment of the iodide showing paramagnetism of 3.13 B.M. before heating changes to 2.25 B.M. in the form of a pale brown product, whose value is considerably lower than those of the normal paramagnetic octahedral or five-coordinated nickel(II) complexes.

The electronic spectra of the iodide before and after dehydration are compared in Fig. 7. The pattern of the product slightly resembles those of octahedral complexes, but a square planar structure may also be somewhat responsible for it, particularly for the absorption band of 22×10^3 cm^{-1}. It is reasonable to consider the complicated spectral pattern as resulting from the contribution of both the octahedral and square planar structures. The same discussion will be applied to the interpretation of the subnormal magnetic moment value. Consequently, the product seems to be a mixture of square planar and octahedral diacido complexes.

Variations in isothermal temperature or heating rate appear to change sparingly a proportion of the square planar and octahedral complexes involved in the product, judging from their color and magnetic moments. The heating condition of preparing preferentially only one of the two structures is not yet established. However, it is confirmable that the slower the heating rate or lower the isothermal temperature, the more the square planar form is favored in the product.

Effect of selection of butanediamines or counter ions upon structural transformation

The proposed thermal transformation from square planar to octahedral structure on the basis of anation was confirmed in the four complexes, [Ni(m-bn)$_2$](NO$_3$)$_2$, [Ni(i-bn)$_2$]Cl$_2$, [Ni(dl-bn)$_2$]Cl$_2$, and [Ni(dl-bn)$_2$]Br$_2$, of 15 complexes prepared, although in the latter two, the transfer can be observed after the thermal dehydration of the respective diaqua complexes.

Table 3 gives the enthalpy changes and the initiation temperatures of the reactions estimated by their DSC peak areas. It is interesting that these reactions proceed endothermically and require a slight enthalpy change of about 10–20 kJ mole^{-1}. The difference in initiation temperature between the

TABLE 3

Enthalpy changes and initiation temperatures of transformation

Original complex	ΔH(kJ mole^{-1})	Initiation temp. (°C)
[Ni(dl-bn)$_2$]Cl$_2$	17.6	159
[Ni(dl-bn)$_2$]Br$_2$	16.0	175
[Ni(i-bn)$_2$]Cl$_2$	11.8	165
[Ni(m-bn)$_2$](NO$_3$)$_2$	9.7	188

corresponding chloride and bromide as shown in Table 3 and that of the practical ease of transformation will be supported by the fact that the smaller counter ion is advantageous for the anation in the order Cl > Br > I.

The selection of butanediamines also shows an obvious effect for the possibility of the reaction, which is probably due to the difference in the conformational structures of coordinated diamines. In the complexes containing 2 moles of butanediamines with a square planar structure, four C-substituted methyl groups are all able to be directed to the equatrial position in dl-bn complexes, whereas at least two of four methyl groups are able to be directed to the axial position in m-bn and i-bn complexes. The latter conformation is found to generate a steric hindrance for the apical position, preventing the approach of the counter ion to a central metal ion to cause a lowering of the reactivity, square planar to octahedral transformation, in m-bn and i-bn complexes.

Nevertheless, the above discussion on ionic radii of counter ions and conformation of diamines may not be applied to the occurrence of the reaction in m-bn nitrate. The peculiarity of the nitrate showing such a transformation has been shown in the other investigations [10,11] dealing with the imine derivatives instead of diamines. In m-bn nitrate, the transformation can be observed at relatively higher temperatures than the other salts. There is a pre-requisite that the complexes are thermally stable at least until the temperature of the start of the transformation. The fact that the transformation can be observed only in the nitrate of the m-bn complex, and not in other complexes of dl-bn and i-bn, seems to be attributable partially to the higher decomposition temperature in m-bn complexes than the other butanediamine complexes, usually by about 20–30°C, by comparing the corresponding salts. An additional stabilization effect (not evident at present) during the rearrangement of the crystal, e.g. hydrogen bonding, is thought to play an important part in the speciality of nitrate.

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