Thermal Square Planar-to-Octahedral Transformation of Nickel(II) Complexes Containing 2-Aminobenzimidazole in the Solid Phase[1)]

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Thermal reactions of the complexes, $[Ni(abi)_4]X_2 \cdot nH_2O$ (abi, 2-aminobenzimidazole; X, Cl, Br, I, NO_3, ClO_4, or $1/2SO_4$; *n*, 3 for chloride and bromide, 1 for nitrate, and 0 for others) were investigated. Distinct color changes from orange to green were observed in the three complexes of chloride, bromide, and nitrate upon heating. It was found from the changes in absorption and far-IR spectra and magnetic susceptibilities under the thermal reactions that the complexes undergo transformation from square planar to tetragonally distorted octahedral structures, involving an increase in the coordination number from four to six. No such transformation could be found in the corresponding iodide, perchlorate, and sulfate. The effect of the introduced amino group on the structural conversion reactions of the abi complexes is discussed as compared with the corresponding benzimidazole complexes, $[Ni(bimd)_4]X_2$, which underwent transformation from square planar to octahedral structure upon heating when X is I or NO_3.[2)]

Nickel(II) ion forms complexes of various structures, *e.g.*, octahedral, tetrahedral, and square planar structures, depending on the ligand, mutual transformation often occurring among them.[3)] Few studies in the solid phase, however, are known.

Tsuchiya *et al.* reported the structural transformation of $[Ni(H_2O)_2(NN\text{-deen})_2]X_2$, where *NN*-deen is *N,N*-diethylethylenediamine and X halide ion.[4)] The chloride, upon heating, evolved two moles of coordinated water accompanied by anation of chloride ions with retention of the original octahedral structure, whereas the bromide underwent transformation from octahedral to square planar structure without anation of bromide ions after the liberation of water molecules. In addition to nickel(II) complexes containing *N*-substituted diamine, the thermal behavior of the complexes with the *C*-substituted diamines, 2-methyl-1,2-propanediamine and 1,2-diphenylethylenediamine, has been studied in the solid phase by Farago *et al.*[5)] and Lifschitz *et al.*,[6)] respectively. Transformation from octahedral to square planar structure was also observed in these complexes. The studies deal with the structural transformation of nickel(II) complexes containing diamine derivatives, accompanied by the change of the coordination number from six to four, upon heating in the solid phase.

Interesting thermal, mutual transformations have been reported as regards spectral measurements. The structure of bis(*N,N*-diethylethylenediamine)copper(II) tetrafluoroborate, perchlorate, and nitrate turns to square planar with fall in temperature, and to octahedral with rise in temperature.[7)] Tsuchiya *et al.* found a new transformation from square planar to octahedral structure in the benzimidazole complexes, $[Ni(bimd)_4](NO_3)_2 \cdot 2.5C_2H_5OH$ and $[Ni(bimd)_4]I_2$, in the solid phase.[2)] The study is characterized by the reactions involving the increase in the coordination number from four to six upon heating, and by the use of imine derivatives as the ligand which acts as a unidentate one.

The present study was undertaken to prepare the square planar nickel(II) complexes containing 2-aminobenzimidazole, and to investigate their thermal transformation into octahedral structure in the solid phase, and the effect of the amino group introduced to benzimidazole on the thermal reactions.

Experimental

Preparation. The ligand, 2-aminobenzimidazole, and the nickel (II) complexes were prepared by the methods reported,[8,9)] their chemical formulas being identified by elemental analyses and spectral measurements.

Thermal Analysis. TG and DSC measurements were carried out with a Rigaku Denki standard TG-DSC apparatus. All the measurements were carried out under constant flow of nitrogen at a heating rate 1.25 °C min^{-1}.

Isothermal Measurements. The green products were obtained by isothermal heating using the electrical 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 IR-F far-infrared spectrophotometer.

Measurements of Magnetic Susceptibilities. 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 a reference material. The susceptibilities of the complexes were corrected by using Pascal's constants for each element or atomic group contained.

Results and Discussion

Thermal Analyses. Since a distinct color change from orange to green was found for the three complexes, chloride, bromide, and nitrate, by the qualitative thermal technique, thermal analyses were carried out by TG-DSC measurements. The results are shown in Figs. 1—3. On the other hand, the iodide, perchlorate, and sulfate complexes decomposed without obvious color change upon heating.

Chloride turns from orange to green at the endothermic peak near 215 °C, at which melting seems to occur (Fig. 1). The exothermic peak near 150 °C seems to be attributable to a slight change in the packing of the crystal, since the changes in color and thermo-

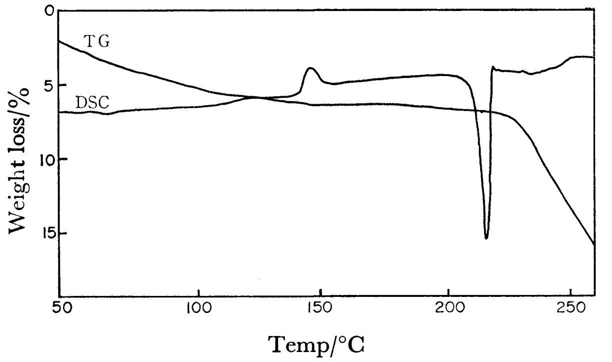

Fig. 1. Thermal analysis of $[Ni(abi)_4]Cl_2 \cdot 3H_2O$.

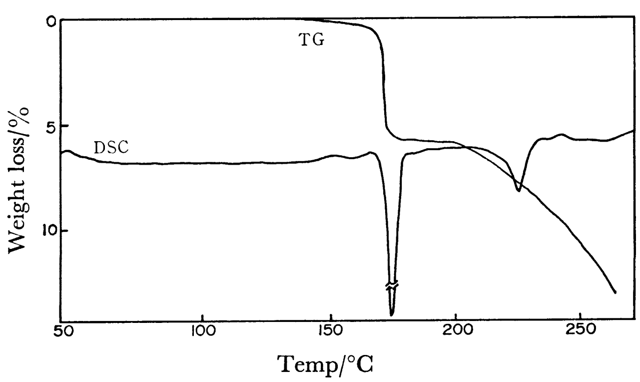

Fig. 2. Thermal analysis of $[Ni(abi)_4]Br_2 \cdot 3H_2O$.

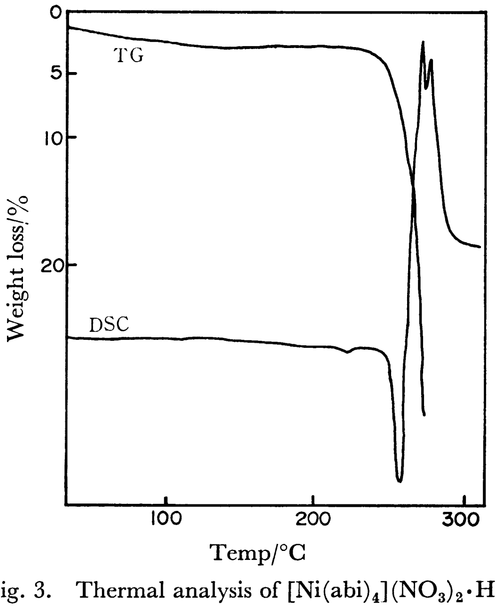

Fig. 3. Thermal analysis of $[Ni(abi)_4](NO_3)_2 \cdot H_2O$.

gravimetric curve are scarcely found in the complex at temperatures lower and higher than that of the peak. Bromide was converted into green completely at 175 °C, accompanied by the liberation of three moles of lattice water, decomposing gradually (TG curve, Fig. 2). For nitrate, no plateau predicting the formation of the stable product was observed (TG curve, Fig. 3), moss-green product being obtained by means of isothermal technique. The endothermic peak involving melting just before the exothermic peak appears with abrupt weight loss near 250 °C seems to indicate simultaneous occurrence of the structural transformation.

The most suitable conditions of isothermal heating for obtaining the products for identification of their structures are as follows: at 200 °C for 2—3 min, at 170 °C for 4—5 min, and at 230 °C for 2—3 min for chloride, bromide, and nitrate, respectively.

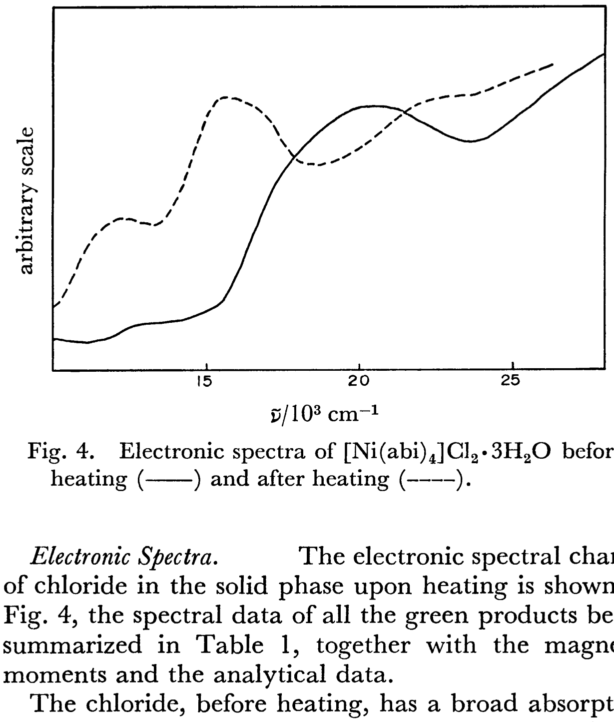

Fig. 4. Electronic spectra of $[Ni(abi)_4]Cl_2 \cdot 3H_2O$ before heating (——) and after heating (– – –).

Electronic Spectra. The electronic spectral change of chloride in the solid phase upon heating is shown in Fig. 4, the spectral data of all the green products being summarized in Table 1, together with the magnetic moments and the analytical data.

The chloride, before heating, has a broad absorption band near 20×10^3 cm^{-1} due to the square planar structure of nickel(II) complexes, and a charge transfer band characteristic to the complexes containing imidazole derivatives (Fig. 4). After heating, the chloride shows three absorption bands in visible region, but they slightly deviate from the general feature of the spectral pattern of octahedral nickel(II) complexes. This is similar to the case of $[Ni(NCS)_2(abi)_4]$ considered to have a tetragonally distorted octahedral structure[9]

TABLE 1. ELECTRONIC SPECTRA DATA, MAGNETIC MOMENTS, AND ANALYTICAL DATA OF THE HEATED PRODUCTS

Products	C(%)		H(%)		N(%)		Absorption Maxima ($\tilde{\nu}/10^3$ cm^{-1})	μ_{eff}(B.M.)
	Found	Calcd	Found	Calcd	Found	Calcd		
$[NiCl_2(abi)_4] \cdot H_2O$	49.48	49.44	4.33	4.45	24.64	24.71	12.5w 16.3 23.1sh	1.98
$[NiBr_2(abi)_4]$	46.55	44.77	3.56	3.76	23.44	22.38	12.5w 16.4 22.5sh	1.56
$[Ni(NO_3)_2(abi)_4] \cdot H_2O$	46.21	45.85	3.79	4.13	26.90	26.74	12.4w 16.5 23.4sh	2.12
$[Ni(NCS)_2(abi)_4]$							13.3w 16.3 22.2sh 26.5	

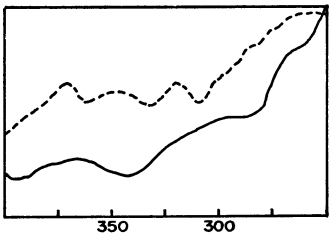

Fig. 5. Far-IR spectra of $[Ni(abi)_4](NO_3)_2\cdot H_2O$ before heating (——) and after heating (----).

(Table 1). Some of the octahedral benzimidazole complexes, $[NiX_2(bimd)_4]$, prefer tetragonal distortion.[10] All the products are expected to have the same structure.

Far-IR Spectra. Figure 5 shows the far-IR spectra of nitrate before and after heating. A distinct difference in their spectra lies in the appearance of the peak at 310 cm^{-1} after heating. Ferraro and Walker[11] 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 owing to the coordination of nitrate ion to central metal. The new peak, appearing in the nitrate heated can be ascribed to $Ni-O(NO_3)$ stretching vibration. If so, the nitrate ions situated in the outer sphere before heating approach the central metal making the coordinated bond in the product.

Magnetic Moments. The magnetic moments of the products are given in Table 1. The complexes, showing diamagnetism before heating, are converted into paramagnetic ones upon heating. The values 1.56—2.12 BM are considerably lower than those of the nomal paramagnetic octahedral nickel(II) complexes. However, the values for the tetragonally distorted octahedral structures fall below 2.0 BM.[12] The data of magnetic moments together with the results of the electronic spectra suggest the formation of the tetragonally distorted octahedral complexes by thermal treatment.

Thermochromism of the three complexes, chloride, bromide, and nitrate, from orange to green is considered to result from the structural transformation from square planar to octahedral structures, involving considerably tetragonal distortion. The transformation can be represented by the following scheme.

$$[Ni(abi)_4]X_2\cdot nH_2O \xrightarrow[\Delta]{-nH_2O} [NiX_2(abi)_4]$$

$$(X=Cl,\ Br,\ NO_3)$$

The analytical data of the products (Table 1) give no confirmation on the decomposition of 2-aminobenzimidazole in coordination sphere upon heating.

One mol of the lattice water appearing in the products of chloride and nitrate is that adsorbed when the products are placed at room temperature. They give the weight loss corresponding to 1 mol of water when heated again at 50 °C.

Enthalpy Changes. The enthalpy changes and the reaction temperatures of the structural transfer reactions determined by the DSC analyses are given in Table 2. Though all the reactions proceed endothermically, no reversibility of the transfer reactions was observed.

TABLE 2. ENTHALPY CHANGES AND REACTION TEMPERATURES

Starting complexes	ΔH(kJ/mol)	Reaction temp/°C
$[Ni(abi)_4]Cl_2\cdot 3H_2O$	8.8	215
$[Ni(abi)_4]Br_2\cdot 3H_2O$	8.8	175
$[Ni(abi)_4](NO_3)_2\cdot H_2O$	7.1	250

The enthalpy changes seem too small for bromide to be caused by the dehydration of three moles of the lattice water alone. It can be explained in terms of the simultaneous occurrence of the structural transformation presumed to proceed exothermically besides the dehydration reaction. In the case of chloride and nitrate the enthalpy changes can be interpreted to be due to the structural transfer reactions being accompanied by endothermic melting.

TABLE 3. POSSIBILITY OF SQUARE PLANAR-TO-OCTAHEDRAL TRANSFORMATION

X	bimd	abi
Cl	(not prepared)	possible
Br	(not prepared)	possible
I	possible	decomposed
NO_3	possible	possible
ClO_4	decomposed	decomposed
SO_4	(not prepared)	decomposed

Comparison with bimd Complexes. The possibilities of the transformation from square planar structure to octahedral one of bimd and abi complexes by the thermal treatment are summarized in Table 3. One striking difference between bimd and abi complexes is the possibility of formation of the square planar structure in the latter complexes containing chloride or bromide ion. The green octahedral dihalogenotetrakis (benzimidazole) complexes were prepared without appearance of the square planar structure for the chloride or bromide, whereas the complexes containing the iodide or nitrate ion were converted from square planar structure into the octahedral diacido complexes by thermal treatment. The results suggest that the ionic radii of anions in bimd complexes are important in stereochemical requirement for the preparation of the starting complexes and structural transformation, *viz.*, the smaller ion fits to a greater extent the packing of the *trans* sites of the coordination plane surrounded by the four bimd molecules.

The square planar species are formed in abi complexes. This seems to depend on steric hinderance by the amino group introduced and on the higher basicity in the abi ligand surrounding a nickel(II) ion. Another feature of the abi complexes is that thermal structural transformation prefers tetragonal distortion in the products heated than in the bimd complexes.

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