

Thermal Square Planar-to-octahedral Transformation of Nickel(II) Complexes Containing 1,2-Diphenyl-1,2-ethanediamine in the Solid Phase

Yoshinori IHARA* and Ryokichi TSUCHIYA†

Laboratory of Chemistry, Faculty of Education, Kanazawa University, Kanazawa 920

†Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

(Received January 5, 1984)

The following ten nickel(II) complexes with *meso*- or *dl*-1,2-diphenyl-1,2-ethanediamine (abbreviated as *meso*-stien and *dl*-stien, respectively) were prepared, and their thermal behavior was investigated in the solid phase: $[\text{Ni}(\text{meso-stien})_2]\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NO}_3$, or ClO_4), $[\text{Ni}(\text{dl-stien})_2]\text{X}_2$ ($\text{X}=\text{I}$ or ClO_4), and $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2]\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$, or NO_3). The square planar bis(*dl*-stien) complex chloride, bromide, and nitrate obtained by thermal dehydration of their respective octahedral diaqua complexes were found by various techniques to be transformed, upon further heating, to the octahedral diacido bis(*dl*-stien) complexes. The complexes containing *dl*-stien have a stronger tendency to show such structural transformations than those containing *meso*-stien. The reason for this difference is discussed.

Nickel(II) ion forms complexes with various structures, e.g. octahedral, tetrahedral, and square planar, depending upon the nature of the ligands, and mutual transformation among these structures often occurs in solution.^{1,2} Up to the present, however, a few studies^{3–5} have dealt with the thermal reaction of octahedral diaqua complexes, $[\text{Ni}(\text{H}_2\text{O})_2(\text{diamine})_2]\text{X}_2$, in the solid phase. These complexes were found to lose $2\text{H}_2\text{O}$ upon heating to form either square planar bis-diamine complexes by mere deformation or octahedral diacido complexes by anation of counter ions.

An interesting example of thermal transformation from the square planar to the octahedral geometry was found in the anation of $[\text{Ni}(\text{bimd})_4](\text{NO}_3)_2 \cdot 2.5\text{C}_2\text{H}_5\text{OH}$, where bimd denotes benzimidazole.⁶ Similar transformations were also reported for the nickel(II) complexes with 2-aminobenzimidazole⁷ and 2,3-butanediamines.⁸ The purpose of the present study is to find whether or not the nickel(II) complexes with stien undergo the thermal square planar-to-octahedral transformation in the solid phase depending upon the structure of stiens and counter anions. Another purpose is to confirm the stronger tendency toward the transformation of the complexes with *dl*-stien than those with *meso*-stien, which was found for the complexes of *dl*- and *meso*-2,3-butanediamine.⁸

Experimental

Preparation. The ligands, *meso*-stien and *dl*-stien, were obtained by the methods described in the literature.^{9,10}

Aqueous solutions of nickel(II) chloride, bromide, iodide, nitrate, or perchlorate were added to ethanolic solutions of the ligands in the molar ratio of 1:2 to prepare the desired bis-type complexes. The resulting yellow or violet crystals were collected by filtration and washed with ethanol and diethyl ether. The formulas determined by elemental analyses and also by spectral and magnetic measurements (Table 1) are as follows: $[\text{Ni}(\text{meso-stien})_2]\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NO}_3$, or ClO_4), $[\text{Ni}(\text{dl-stien})_2]\text{X}_2$ ($\text{X}=\text{I}$ or ClO_4), and $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2]\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}$, or NO_3).

Measurements. Simultaneous TG and DSC measurements were carried out with a Rigaku Denki standard TG-DSC apparatus under a constant flow of nitrogen. The heating rates and amounts of samples used are given in Fig. 1. The complexes shown in Table 2 were obtained by isothermal heating at the temperatures corresponding to the respective DSC peaks.

The electronic spectra in the solid phase were measured by the diffuse reflectance method on a JASCO UNIDEC-410 spectrophotometer. The effective magnetic moments were evaluated from the susceptibilities measured by Gouy's method at room temperature.

Results and Discussion

Thermal Analyses. Of the ten complexes studied, all the yellow *meso*-stien complexes, and *dl*-stien iodide and perchlorate, did not show expected color changes. Heating of the remaining three diaqua complexes, however, led to an irreversible thermochromism consisting of two steps from violet to blue through yellow before decomposition.

The results of the simultaneous TG-DSC measure-

TABLE 1. DATA ON THE ELEMENTAL ANALYSES, ELECTRONIC SPECTRA AND MAGNETIC MOMENTS OF THE ORIGINAL COMPLEXES

Complexes	Color	Analytical data ^{a)}			Absorption maxima $\bar{\nu}/10^3 \text{ cm}^{-1}$	μ_{eff} BM
		H(%)	C(%)	N(%)		
$[\text{Ni}(\text{meso-stien})_2]\text{Cl}_2$	yellow	5.80(5.82)	60.45(60.68)	10.12(10.11)	22.5	diamag.
$[\text{Ni}(\text{meso-stien})_2]\text{Br}_2$	yellow	5.07(5.02)	52.33(52.30)	8.70(8.71)	22.3	diamag.
$[\text{Ni}(\text{meso-stien})_2]\text{I}_2$	yellow	4.36(4.38)	45.49(45.63)	7.67(7.60)	22.1 sh	diamag.
$[\text{Ni}(\text{meso-stien})_2](\text{NO}_3)_2$	yellow	5.31(5.31)	55.46(55.38)	13.63(13.84)	22.6	diamag.
$[\text{Ni}(\text{meso-stien})_2](\text{ClO}_4)_2$	yellow	4.70(4.73)	49.30(49.30)	8.04(8.21)	22.5	diamag.
$[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2]\text{Cl}_2$	violet	5.96(6.15)	56.86(56.98)	9.42(9.49)	13.5 18.5 27.7 sh	3.30
$[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2]\text{Br}_2$	violet	5.31(5.34)	49.25(49.52)	8.51(8.25)	13.7 18.3 27.8 sh	3.31
$[\text{Ni}(\text{dl-stien})_2]\text{I}_2$	yellow	4.17(4.38)	45.37(45.63)	7.58(7.60)	22.2	diamag.
$[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2](\text{NO}_3)_2$	violet	5.35(5.64)	51.40(52.28)	12.98(13.06)	13.5 18.3 27.6 sh	3.33
$[\text{Ni}(\text{dl-stien})_2](\text{ClO}_4)_2$	yellow	4.96(4.73)	49.28(49.30)	8.28(8.21)	22.1	diamag.

a) Calculated values are in parentheses.

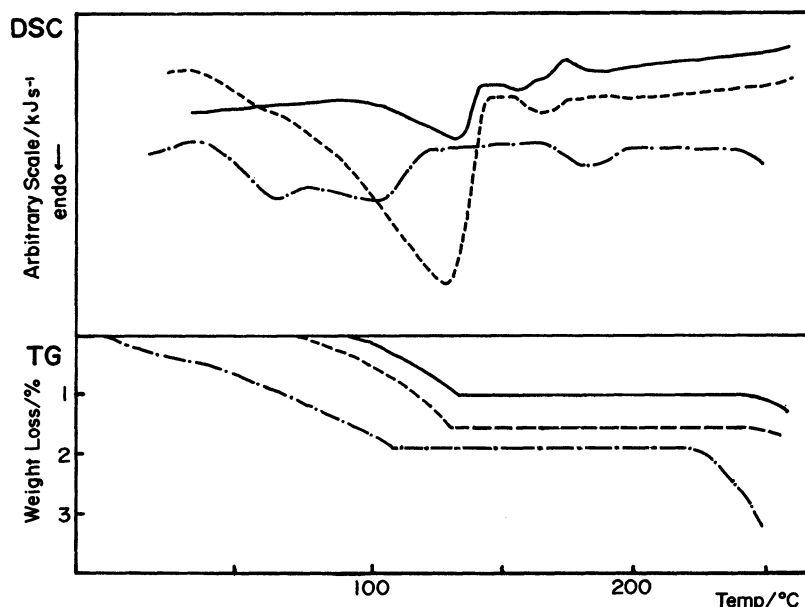


Fig. 1. TG-DSC patterns of $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2]\text{Cl}_2$ (—), $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2]\text{Br}_2$ (-----), and $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2](\text{NO}_3)_2$ (— · —). The heating rate and amount of sample used were as follows: $1.25^\circ\text{C min}^{-1}$, 17.5 mg for chloride, $2.5^\circ\text{C min}^{-1}$, 40.4 mg for bromide, and $1.25^\circ\text{C min}^{-1}$, 32.5 mg for nitrate, respectively.

TABLE 2. DATA ON THE ELEMENTAL ANALYSES, ELECTRONIC SPECTRA, AND MAGNETIC MOMENTS OF THE COMPLEXES OBTAINED BY HEATING

Complexes	Color	Analytical data ^{a)}			Absorption maxima		μ_{eff}
		H(%)	C(%)	N(%)	$\bar{\nu}/10^3\text{ cm}^{-1}$		B M
[Ni(<i>dl</i> -stien) ₂]Cl ₂	yellow				22.7		diamag.
[NiCl ₂ (<i>dl</i> -stien) ₂]	blue	5.57(5.82)	61.32(60.68)	10.16(10.11)	14.3	17.9 26.5 sh	3.28
[Ni(<i>dl</i> -stien) ₂]Br ₂	yellow				22.5		diamag.
[NiBr ₂ (<i>dl</i> -stien) ₂]	blue	5.16(5.02)	52.16(52.30)	8.81(8.71)	13.9	18.1 26.1 sh	3.33
[Ni(<i>dl</i> -stien) ₂](NO ₃) ₂	yellow				22.9		diamag.
[Ni(NO ₃) ₂ (<i>dl</i> -stien) ₂]	blue	5.43(5.31)	54.34(55.38)	13.55(13.84)	14.3	18.4 26.6 sh	3.22

a) Calculated values are in parentheses.

ments are shown in Fig. 1. The weight losses in TG curves correspond to two moles of coordinated water (obsd 6.06%, calcd 6.10% for chloride; 4.11%, 5.31% for bromide; and 5.85%, 5.60% for nitrate). The dehydration proceeds endothermically; thereafter, a small endothermic peak appears at 145°C , 150°C , and 170°C for the chloride, bromide, and nitrate, respectively, without any change in TG curves. The yellow complexes obtained by the loss of the coordinated water were converted to blue after the second endothermic peaks, which indicated the thermochromism from violet to blue through yellow.

Cooling of the blue products did not cause the reverse color change. However, the yellow products absorbed water molecules relatively easily in the coordination sphere, and after cooling and standing in the air for several hours, they changed completely to the original octahedral complexes. This change was confirmed by the data of elemental analyses, electronic spectra, and magnetic moments.

The exothermic peak observed only for the chloride at 172°C did not seem to correspond to a fundamental structural change, because the complex did scarcely show any color change, and the IR spectra measured at 165°C and 180°C , i.e. before and after the peak, were

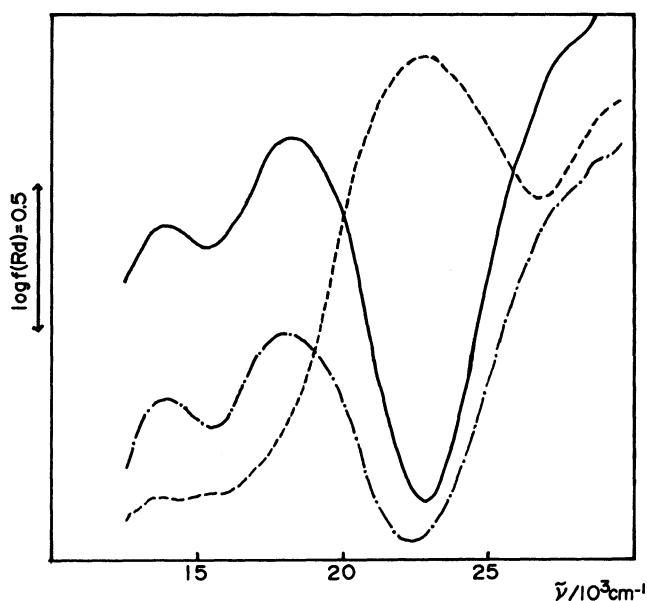


Fig. 2. Electronic spectra of $[\text{Ni}(\text{H}_2\text{O})_2(\text{dl-stien})_2]\text{Br}_2$ before heating (—) and after heating at 120°C (-----) and at 170°C (— · —).

TABLE 3. THE ENTHALPY CHANGES AND INITIATION TEMPERATURES OF THE SQUARE PLANAR-TO-OCTAHEDRAL TRANSFORMATION

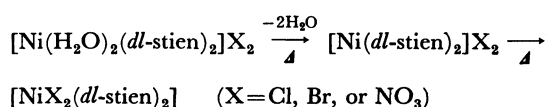
X \ NN	<i>dl</i> -stien	<i>meso</i> -bn ^{a)}	<i>dl</i> -bn ^{a)}
Cl	4.1 kJ/mol 145°C		17.6 kJ/mol 159°C
Br	2.4 kJ/mol 150°C		16.0 kJ/mol 175°C
NO ₃	10.0 kJ/mol 170°C	9.7 kJ/mol 188°C	

nearly the same.

Electronic Spectra. The electronic spectra corresponding to the color change of the solid bromide upon heating are shown in Fig. 2. The spectral data are summarized in Table 2, together with the magnetic moments and analytical data.

The blue product has a spectral pattern identical with that of the original octahedral structure. On the other hand, the pattern of the yellow product, which is completely different from others, coincides with that of characteristic square planar nickel(II) complexes which have usually a broad and strong absorption band in the same frequency region. The chloride and nitrate show similar changes in the absorption spectra (Table 2).

Magnetic Moments. The yellow products are diamagnetic, whereas the blue products paramagnetic (3.22–3.33 BM). These facts, together with the above absorption spectral data, suggest that the yellow and blue products are the square planar and octahedral complexes, respectively. The stepwise thermochemical changes observed for the three diaqua *dl*-stien complexes are represented by the following scheme:



Comparison with the Butanediamine Complexes.

In Table 3 the enthalpy changes and the initiation temperatures of the square planar-to-octahedral transformation estimated from the DSC peaks are compared with those of the corresponding 2,3-butanedi-amine (bn) complexes. The blank space in the Table means the absence of the transformation. The data show that the heat required to cause the transformation is smaller for the stien complexes than for the bn complexes.

In conclusion, the present study confirmed the stronger tendency of the complexes containing the *dl*-form toward the square planar-to-octahedral transformation than those of the *meso*-form. It was also found that the smaller anion is more advantageous for the configurational change, *i. e.* the order, Cl⁻ > Br⁻ > I⁻ holds for the complex halides.

The nitrate complexes seem to have a somewhat higher inclination to cause the transformation irrespective of the ligand configuration (*meso*- or *dl*-), as was recognized for benzimidazole⁶⁾ and 2-aminobenzimidazole.⁷⁾ Additional stabilization due to the formation of hydrogen bonding between nitrate ion and diamines during the thermal structural change seems to be a plausible reason for the special property of the nitrate complex.

The discussion developed in the preceding paper⁸⁾ can be applied similarly to the difference in reactivity between the *meso*- and *dl*-stien complexes. In the *dl*-stien complexes containing two moles of stien with a square planar structure, four phenyl groups are able to occupy the equatorial positions, whereas for the *meso*-stien complexes at least two of four phenyl groups are forced to occupy the axial positions. The latter conformation will make the apical approach of the counter ion to the central metal ion difficult because of the steric hindrance.

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