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Studies of the Metal Complexes of Cyclohexane Derivatives. VI.[1) The Thermal Transformation of Nickel(II) Complexes of 1,2-Cyclohexanediamine Isomers

Reiko SAITO* and Yoshinori KIDANI†

Aichi Junior College of Nursing, Kamishidanmi, Moriyama-ku, Nagoya 463

†*Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabedori, Mizuho-ku, Nagoya 467*

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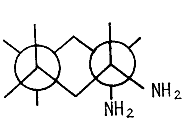
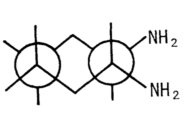
The thermal transformations of the following three types of nickel(II) complexes were investigated by means of TG-DSC analyses: $[Ni(t\text{-chxn})_2(H_2O)_2]X_2$, $[Ni(c\text{-chxn})_3]X_2 \cdot nH_2O$, and $[Ni(t\text{-chxn})_3]X_2 \cdot nH_2O$ ($X = Cl^-$, Br^-, and NO_3^-), where *c*- and *t*-chxn denote *cis*- and *trans*-1,2-cyclohexanediamine respectively. The distorted octahedral $[Ni(t\text{-chxn})_2(H_2O)_2]X_2$ complexes ($X = Cl^-$ and Br^-) are thermally deaquated to form yellow complexes, which then turn into parental diaquabis-complexes in the air at room temperature. $[Ni(t\text{-chxn})_2(H_2O)_2](NO_3)_2$ undergoes a thermal deaquation-anation reaction. The octahedral tris(*c*-chxn) complex is converted into a square planar bis(*c*-chxn) one by the evolution of one molecule of the ligand upon heating, whereas tris(*t*-chxn) complex became a distorted octahedral bis(*t*-chxn) one with anion coordination. In this paper, the stereochemical thermal changes of the complexes in the solid state will be discussed with regard to the steric configuration of the ligands.

The present authors reported earlier the preparations of the copper(II) and the nickel(II) complexes of *cis*- and *trans*-1,2-cyclohexanediamine (abbreviated as *c*-chxn and *t*-chxn), and showed that the structures of the bis-complexes were greatly affected by the steric configurations of these diamines.[2) The ligand, *t*-chxn, whose amino groups bonded to the cyclohexane ring in the diequatorial conformation(b), as is shown below, can be expected to have a coordination ability closely related to that of ethylenediamine.[3–5) It affords violet paramagnetic bis-complexes such as $[Ni(t\text{-chxn})_2(H_2O)_2]Cl_2$. On the other hand, since the *c*-chxn has two amino groups in the axial and the equatorial positions (a), it preferentially forms yellow diamagnetic bis-complexes such as $[Ni(c\text{-chxn})_2]Cl_2$. The distances between N atoms of the diamine isomers are nearly equal, therefore, the structural differences among the complexes seem to be due to the degree of the steric hindrance of the cyclohexane ring. In this paper, the results of thermal reactions of the nickel(II) complexes in the solid state will be described and the steric influence of these ligands on coordination will be shown.



(a) *c*-chxn



(b) *t*-chxn

Experimental

Measurements. Thermogravimetric(TG) and differential scanning calorimetric(DSC) curves were obtained with a Rigaku Denki 8185 Dl apparatus at a 1.25 °C min^{-1} heating rate and with a 50 cm^3 min^{-1} flow rate of nitrogen gas. The reflectance spectra were measured with a Hitachi EPS-3T spectrophotometer. The infrared spectra were recorded with a JASCO IRA-2 spectrophotometer by means of the HCB mull and the KBr disc method.

Preparations. The ligands, *c*-chxn and racemic *t*-chxn, were obtained in the manner reported previously.[6) $[Ni(t\text{-chxn})_2(H_2O)_2]Br_2$, $[Ni(c\text{-xhn})_3]Cl_2 \cdot 1.5H_2O$, $[Ni(c\text{-chxn}_3)]Br_2 \cdot H_2O$, and $[Ni(c\text{-chxn})_3](NO_3)_2 \cdot 0.5H_2O$ were prepared by means of the previously described procedures.[2) $[Ni(t\text{-chxn})_2(H_2O)_2]X_2$ ($X = Cl^-$ and NO_3^-), $[Ni(t\text{-chxn})_3]Cl_2 \cdot 2H_2O$, and $[Ni(t\text{-chxn})_3]Br_2 \cdot 3H_2O$ were synthesized with reference to the methods described in the literature.[7,8) The chemical formulae were confirmed by elemental analyses.

Results and Discussion

The TG-DSC curves of the following three types of complexes, $[Ni(t\text{-chxn})_2(H_2O)_2]X_2$, $[Ni(c\text{-chxn})_3]X_2 \cdot nH_2O$, and $[Ni(t\text{-chxn})_3]X_2 \cdot nH_2O$ ($X = Cl^-$, Br^- and NO_3^-), are shown in Figs. 1, 2, and 3 respectively, while the results are summarized in Table 1. It was confirmed that the colors of $[Ni(c\text{-chxn})_2]X_2$ complexes did not change in the temperature range from *ca.* 25 °C to 250 °C. Therefore, the square planar structures of these complexes are regarded as very stable. The *c*-chxn molecules in this structure make it unfavorable for water molecules or anions to approach the nickel(II) ion along

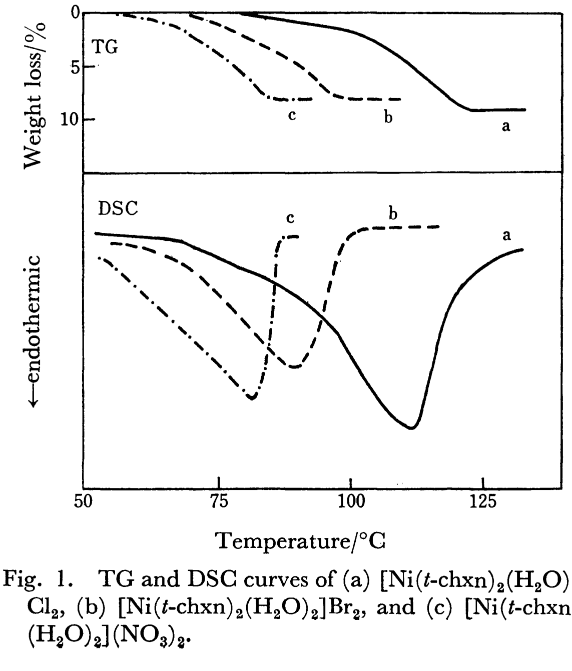


Fig. 1. TG and DSC curves of (a) $[Ni(t\text{-chxn})_2(H_2O)_2]Cl_2$, (b) $[Ni(t\text{-chxn})_2(H_2O)_2]Br_2$, and (c) $[Ni(t\text{-chxn})_2(H_2O)_2](NO_3)_2$.

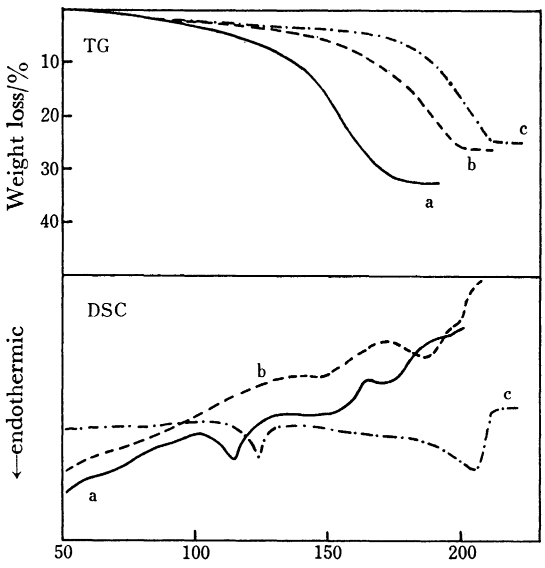


Fig. 2. TG and DSC curves of (a) $[Ni(c\text{-chxn})_3]Cl_2 \cdot 1.5H_2O$, (b) $[Ni(c\text{-chxn})_3]Br_2 \cdot H_2O$, and (c) $[Ni(c\text{-chxn})_3](NO_3)_2 \cdot 0.5H_2O$.

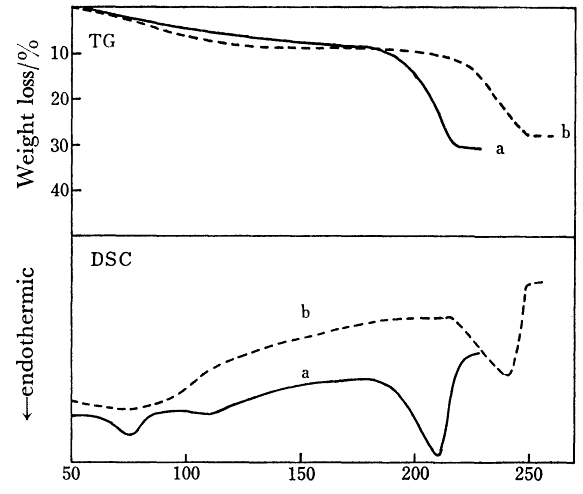


Fig. 3. TG and DSC curves of (a) $[Ni(t\text{-chxn})_3]Cl_2 \cdot 2H_2O$ and (b) $[Ni(t\text{-chxn})_3]Br_2 \cdot 3H_2O$.

the z axes because of the steric hindrance caused by the cyclohexane rings, which are located obliquely above the chelate ring.

The diaquabis(*t*-chxn) complexes of three kinds of X anions liberated two molecules of coordinated water in the following order of increasing deaquation temperature; $X=NO_3^- < Br^- < Cl^-$, giving similar DSC curves. A few qualitative observations of this thermal behavior have been reported by Tsuchida.⁽⁷⁾ The temperature at which thermal deaquation occurs seems to be dependent upon the degree of interaction between a water molecule and an anion, and also upon the degree of axial perturbation of the anions. The present authors have presumed on the basis of the infrared spectra, that, in the structures of these complexes, not anions, but water molecules are coordinated in the apical positions.[2)] The coordination of water molecules is also suggested by the large endothermic peak of the DSC curves.

The complexes of this type are found to undergo thermal transformation in two ways with a variety of anions, like diaquabis(*N*,*N*-diethylethylenediamine)nickel(II) complexes.[9,10)] In the cases of the chloride and the bromide, yellow complexes were obtained after deaquation, but they turned blue violet again when they were kept in the air at room temperature. The resultant blue violet complexes are assumed to be the initial diaquabis-complexes because the former exhibit infrared and electronic spectra almost identical with those of the latter. This indicates the reversible transformation from a square planar structure to a distorted octahedron by the coordination of water molecules in the apical positions in the solid state. On the other hand, the color of $[Ni(t\text{-chxn})_2(H_2O)_2](NO_3)_2$ did not change on deaquation. Figure 4 shows the infrared spectra of the nitrate complex and the sample obtained by heating. The broad ν_{NO} of the initial diaquabis-complex splits into two peaks, at 1310 and 1432 cm^{-1}, after deaquation. They can reasonably be assigned to the ν_{NO} stretching

Table 1. DSC peak temperature (t_m/°C), weight-losses ($-\Delta W$/%), and color changes in thermal analyses

Complexe	Deaquation				Liberation of ligand				Color change
	t_m/°C	DSC	$-\Delta W$/%		t_m/°C	DSC	$-\Delta W$/%		
			Obsd	Calcd			Obsd	Calcd	
$[Ni(t\text{-chxn})_2(H_2O)_2]Cl_2$	112	endo	9.2	9.1					BV→Y
$[Ni(t\text{-chxn})_2(H_2O)_2]Br_2$	90	endo	8.3	7.5					BV→Y
$[Ni(t\text{-chxn})_2(H_2O)_2](NO_3)_2$	82	endo	8.1	8.2					BV→BV
$[Ni(c\text{-chxn})_3]Cl_2 \cdot 1.5H_2O$	—[a)]	endo	—[b)]		115, 156, 174	endo	32.8	28.3	V→Y
$[Ni(c\text{-chxn})_3]Br_2 \cdot H_2O$	—[a)]	endo	—[b)]		149, 188, 197	endo	26.0	22.8	V→Y
$[Ni(c\text{-chxn})_3](NO_3)_2 \cdot 0.5H_2O$	—[a)]	endo	—[b)]		124, 206	endo	25.1	24.0	V→Y
$[Ni(t\text{-chxn})_3]Cl_2 \cdot 2H_2O$	77, 112	endo	7.9	7.1	211	endo	22.5	22.5	V→BV
$[Ni(t\text{-chxn})_3]Br_2 \cdot 3H_2O$	—[a)]	endo	8.9	8.8	240	endo	19.1	18.6	V→BV

endo=endothermic, BV=blue violet, V=violet, Y=yellow

a) The deaquation change occurred so gradually that the DSC peak temperature could not be measured exactly. b) The weight-losses in the deaquation step could not be measured independently, so the ΔW values in the Liberation of ligand column contain ΔW in the deaquation step.

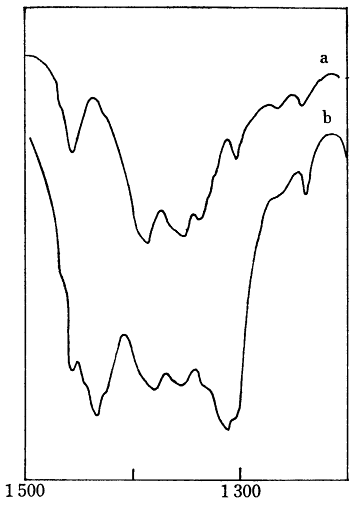


Fig. 4. Infrared spectra of $[Ni(\mathit{t}\text{-chxn})_2(H_2O)_2](NO_3)_2$: (a) before heating, (b) after heating.

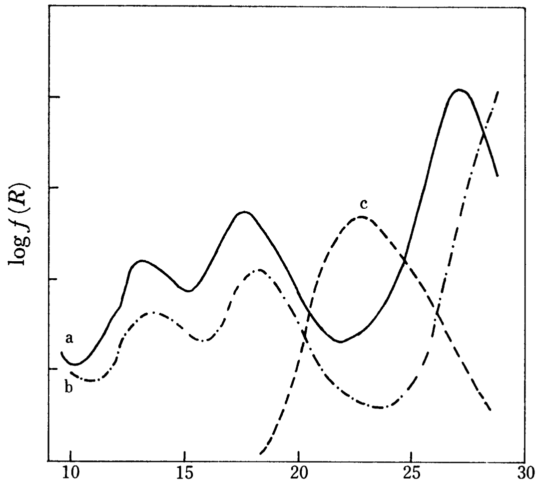


Fig. 5. Reflectance spectra of the samples, after heating, (a) $[Ni(\mathit{t}\text{-chxn})_3]Br_2\cdot 3H_2O$ at 260 °C, (b) $[Ni(\mathit{t}\text{-chxn})_2(H_2O)_2](NO_3)_2$ at 100 °C, and (c) $[Ni(\mathit{c}\text{-chxn})_3]Cl_2\cdot 1.5H_2O$ at 220 °C.

of the unidentate nitrate anion.$^{11)}$ In the reflectance spectrum of the corresponding anhydrous complex, three characteristic maxima, at 12300 (sh), 13500, and 17200 cm^{-1}, were observed (Fig. 5), they are ascribable to the trans tetragonal structure, although the band near 28000 cm^{-1} could not be observed due to the charge-transfer band of a nitrate anion. Therefore, in the case of nitrate, deaquation-anation seems to take place simultaneously. This thermal reaction is parallel to that found by Inoue$^{12)}$ and Curtis$^{11)}$ for $[Ni(en)_2(H_2O)_2](NO_3)_2$.

The tris-complexes of *c*-chxn changed to yellow complexes, liberating some water of crystallization and one molecule of ligand on heating, although no distinct plateau on the TG curves for the deaquation process were observed. The spectral patterns of the yellow complexes are in good agreement with those of the corresponding diamagnetic $[Ni(\mathit{c}\text{-chxn})_2]X_2$.$^{2)}$ Nishimoto reported the thermal transformation from the octahedral structure of tris(*meso*-2,3-butanediamine)nickel(II) halide to a square planar structure.$^{13)}$ It was revealed that the cyclohexane ring of *c*-chxn had steric effects on the configuration of the nickel(II) complexes similar to those of the ethylenediamine derivative with substituents on the C atoms.

The tris-complexes of *t*-chxn with halide ions gave blue violet bis-complexes, releasing one molecule of a ligand, upon heating. The visible reflectance spectra of the resultant bis-complexes show $\nu_{\max}$ at 12100 (sh), 13500, 17500, and 27400 cm^{-1} ($X=Cl^-$), and at 11800 (sh), 13200, 17500, and 27500 cm^{-1} ($X=Br^-$), respectively (Fig. 5). The resemblance of these spectra to those of dihalogenobis(*N*,*N*′-dimethylethylenediamine)nickel(II)$^{14)}$ suggests that the bis-complexes have a tetragonally distorted octahedral structure, with halide ions coordinated in the apical positions. The *t*-chxn is assumed to prefer the above structure because of the ample spaces in the z axes. The corresponding nitrate released a ligand at higher temperatures and gave a brown material as a result of the successive decomposition. It is of interest to note that the temperatures of the eliminating ligand for each type of tris-complex, *c*-chxn and *t*-chxn, increase in the following order; $X=Cl^- < Br^- < NO_3^-$, the reverse of that in the case of the deaquation of diaquabiscomplexes.

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