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Solid-phase thermal reactions of nickel(II) complexes containing *dl*-4-methyl-1,2-pentanediamine

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Abstract

The thermal reactions of bis(*dl*-4-methyl-1,2-pentanediamine)nickel(II) complexes have been studied in the solid phase. A new example of square-planar (low spin) to octahedral (high spin) isomeric transformation was discovered in the chloride. The transformation proceeded endothermically ($\Delta H = 3.50\ \mathrm{kJ\ mol^{-1}}$) and was accompanied by a reversible thermochromism from yellow to violet-blue on heating.

INTRODUCTION

Nickel(II) complexes provide various informative examples of thermochromism in the solid phase, which are mainly associated with a change in coordination geometry [1]. In such complexes, small differences in the electronic properties and steric requirements of the ligands are reflected in the structures that they prefer when heated or cooled. However, a systematic knowledge is still lacking as to the factors that decide the preference of certain coordination geometries at different temperatures. Among several kinds of solid-phase isomeric transformations of nickel(II) complexes already studied, the transformation between a square-planar structure and an octahedral one seems to be of special interest and importance, particularly in relation to the problem of spin equilibrium in solution [2–4].

We have studied the thermal reactions of nickel(II) complexes containing C- or N-substituted ethylenediamines, $[Ni(diamine)_2]X_2$ or $[Ni(H_2O)_2(diamine)_2]X_2$ (where X is Cl^-, Br^-, NO_3^-, or ClO_4^-), in the solid phase [5], and also reported that several complexes with C-substituted ethylenediamines undergo reversible structural isomerization from square-planar to octahedral based on thermal anation [6]. This type of isomerization is accompanied by thermochromism from yellow to blue and by a drastic change in the spin state from low spin (diamagnetic) to high spin

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(approx. 3.0 BM). In continuation of these studies, the solid-phase thermal reactions of bis(*dl*-4-methyl-1,2-pentanediamine)nickel(II) complexes were investigated in the present study.

EXPERIMENTAL

The ligand *dl*-4-methyl-1,2-pentanediamine (*dl*-1-isobutyl-1,2-ethanediamine, *dl*-iben), was prepared as follows. Racemic methyl 2-amino-4-methylpentanoate (DL-leucine methyl ester) was converted into *dl*-2-amino-4-methylpentanamide by the method of Arpesella et al. [7]. Racemic iben was obtained by reducing the amide with $LiAlH_4$ according to the procedure described by Yano et al. [8]. The complexes, *trans*-$[Ni(H_2O)_2(dl\text{-}iben)_2]X_2$ (where X is Cl^-, Br^-, NO_3^-, or ClO_4^-), were prepared by the following method. To an aqueous solution of a nickel(II) salt, $NiX_2 \cdot nH_2O$ (X is Cl^-, Br^-, NO_3^-, or ClO_4^-), a methanolic solution of *dl*-iben was added dropwise in the molar ratio of 1:2. The solutions were allowed to stand for several days to precipitate the desired bis-type complexes. The violet crystals deposited were collected by filtration and washed with ethanol and diethyl ether and analyzed. Found: C, 35.76; H, 9.29; N, 13.87%; calculated for the chloride ($NiC_{12}H_{36}N_4O_2Cl_2$): C, 36.21; H, 9.12; N 14.08%. Found: C, 30.05; H, 7.30; N, 11.62%; calculated for the bromide ($NiC_{12}H_{36}N_4O_2Br_2$): C, 29.60; H, 7.45; N, 11.51%. Found: C, 31.45; H, 8.09; N, 18.53%; calculated for the nitrate ($NiC_{12}H_{36}N_6O_8$): C, 31.95; H, 8.04; N, 18.63%. Found: C, 27.42; H, 7.10; N, 10.74%; calculated for the perchlorate ($NiC_{12}H_{36}N_4O_{10}Cl_2$): C, 27.40; H, 6.90; N, 10.65%.

Simultaneous TG–DTA or DSC measurements were carried out with a Seiko SSC/580 TG/DTA-30 or a Seiko SSC/580 DSC-10 apparatus. The conditions of the runs are given in the appropriate figure. The electronic spectra in the solid phase were measured by the diffuse reflectance method with a Hitachi U-3400 spectrophotometer equipped with a reflection attachment. The spectra at elevated temperatures were monitored by use of a hand-made heating cell, which was set up on the apparatus and was controlled by an REX-C72 temperature controller equipped with a copper–constantan thermocouple.

RESULTS AND DISCUSSION

The electronic spectrum of $[Ni(H_2O)_2(dl\text{-}iben)_2]Cl_2$ is shown in Fig. 1 (together with those of the thermal reaction products, see below). The number of observed bands and the mode of splitting clearly indicate that the complex has a trans-octahedral geometry [9, 10]. The spectra of the other complexes are all similar, leading to the formula, *trans*-$[Ni(H_2O)_2(dl\text{-}iben)_2]X_2$ (X is Br^-, NO_3^-, or ClO_4^-).

Figure 2 shows the results of simultaneous TG–DTA for all the complexes. The abrupt weight losses observed in the TG curves below 80°C and

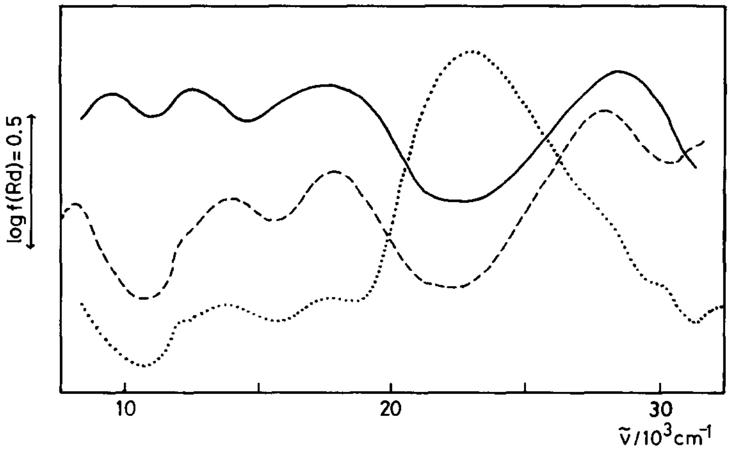

Fig. 1. Electronic spectra of *trans*-$[Ni(H_2O)_2(dl\text{-iben})_2]Cl_2$(——), and the products obtained by heating the trans complex at 70°C (· · ·) and 200°C (– – –).

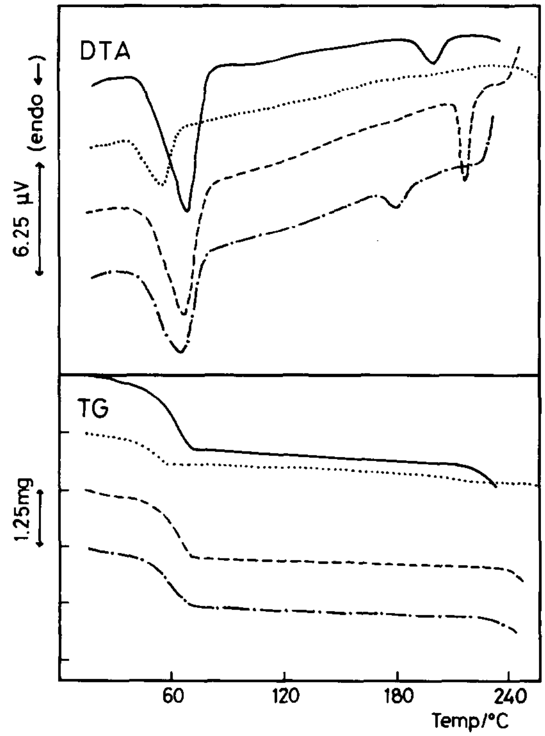

Fig. 2. TG–DTA results for *trans*-$[Ni(H_2O)_2(dl\text{-iben})_2]X_2$, where X is Cl^- (——), Br^- (· · ·), NO_3^- (– – –), and ClO_4^- (— · —), under a constant flow of N_2 at 0.2 dm³ min⁻¹ (heating rate, 5°C min⁻¹ for all runs; sample weight, 15.3, 15.3, 16.6, and 16.7 mg for the chloride, bromide, nitrate, and perchlorate, respectively).

the corresponding endothermic DTA peaks are due to the liberation of two moles of coordinated water molecules (% weight loss: obsd., 9.21%; calcd. for the chloride, 9.05%; 6.76% and 7.40% for the bromide; 8.43% and 7.98% for the nitrate; 7.36% and 6.85% for the perchlorate). In each dehydration step, a pronounced thermochromism is observed for three of the complexes, not the nitrate, as follows: violet → yellow (chloride); violet → violet-blue (bromide); violet → orange (perchlorate). After the dehydration, a small endothermic peak appears at approx. 185–215°C, 209–227°C, and 169–192°C for the chloride, nitrate, and perchlorate, respectively, while the TG curves remain flat. The peaks of the nitrate and perchlorate correspond to the melting points of the complexes. In the case of chloride, the anhydrous yellow complex generated just after dehydration is changed again into a violet-blue species by this endothermic reaction.

The changes in the electronic spectra corresponding to the respective color changes of the chloride are shown in Fig. 1. The violet-blue complex produced at 200°C has a spectral pattern identical with that of the original trans-octahedral species, except for a slight shift in the bands, which indicates a partial exchange of the ligands, while that of the yellow product (at 70°C) is characteristic of a square-planar structure [11]. The overall reaction of the chloride can thus be formulated

$$\textit{trans}\text{-}[\mathrm{Ni}(\mathrm{H_2O})_2(\textit{dl}\text{-iben})_2]\mathrm{Cl_2} \xrightarrow{-2\mathrm{H_2O}} [\mathrm{Ni}(\textit{dl}\text{-iben})_2]\mathrm{Cl_2} \longrightarrow \textit{trans}\text{-}[\mathrm{NiCl_2}(\textit{dl}\text{-iben})_2]$$

The second step of this reaction corresponds to the square-planar to octahedral isomeric transformation.

Table 1 summarizes the spectral data of the diaqua complexes and their thermal reaction products, and the configurational assignments based on the spectral data. The spectral patterns of the bromide and nitrate remain nearly unchanged after dehydration, showing that the trans-octahedral

TABLE 1

Electronic spectral data and configurational assignments

Complex	Temp./°C	Band maxima, $\bar{\nu}/10^3$ cm^{-1}						Configuration
trans-[Ni(H_2O)$_2$(*dl*-iben)$_2$]Cl_2	RT	9.5		12.4		17.5	28.4	Trans-diaqua
	70						22.9	Square planar
	200	8.1		13.9		17.9	27.8	Trans-dichloro
trans-[Ni(H_2O)$_2$(*dl*-iben)$_2$]Br_2	RT	8.4		13.3		17.9	28.1	Trans-diaqua
	100	7.6		13.7		17.9	27.7	Trans-dibromo
trans-[Ni(H_2O)$_2$(*dl*-iben)$_2$](NO_3)$_2$	RT	9.0		12.8	13.5	18.2	28.1 sh	Trans-diaqua
	100	8.3	9.4	12.8	13.5	18.2	28.7	Trans-dinitrato
trans-[Ni(H_2O)$_2$(*dl*-iben)$_2$](ClO_4)$_2$	RT	8.8		12.8	13.5	18.2	28.4	Trans-diaqua
	100						21.9	Square planar

configuration is retained during the thermal reaction. The perchlorate undergoes dehydration to form an orange square-planar complex upon heating, because of the bulkiness and poor coordination ability of ClO_4^-. It is thus clear that the reactions of deaquation–anation (diaqua-octahedral → dianiono-octahedral) and simple deaquation (diaqua-octahedral → square-planar) take place in the former two complexes and the perchlorate, respectively, as shown below

$$trans\text{-}[Ni(H_2O)_2(dl\text{-iben})_2]X_2 \xrightarrow{-2H_2O} trans\text{-}[NiX_2(dl\text{-iben})_2]$$

$(X = Br^-$ or $NO_3^-)$

$$trans\text{-}[Ni(H_2O)_2(dl\text{-iben})_2](ClO_4)_2 \xrightarrow{-2H_2O} [Ni(dl\text{-iben})_2](ClO_4)_2$$

Among the *dl*-iben complexes, only the chloride underwent a thermal square-planar to octahedral isomeric transformation after dehydration. In the course of the violet (diaqua-octahedral) → yellow (square-planar) → violet-blue (dichloro-octahedral) changes, the second change (yellow → violet-blue) is reversible under a nitrogen atmosphere; in open air, however, the anhydrous products (both the yellow and the violet-blue species) absorb water molecules readily to revert to the original violet diaqua complexes within a few minutes. The enthalpy change of the transformation was 3.50 kJ mol^{-1} which was measured in a highly sensitive DSC apparatus: heating rate, 5°C min^{-1}; gas flow, N_2 at 0.1 dm^3 min^{-1}; sample weight, 8.7 mg. This value is somewhat lower than those for the same type of transformations confirmed in other C-substituted ethylenediamine nickel(II) complexes [6, 12]. Unfortunately, because of the rapid reverse reaction on cooling, the change in magnetic moment could not be measured for the thermochromic transformation.

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