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Thermal reactions of nickel(II) complexes containing optically active 1,2-cyclohexanediamine in the solid state and a comparison with those of the corresponding complexes with the racemate

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Abstract

Nickel(II) complexes of *l*-1,2-cyclohexanediamine (*l*-chxn) were prepared, and their thermal behavior was investigated in the solid phase. The original complexes were all violet *trans*-diaquabis(*l*-chxn) complexes (*trans*-$[Ni(H_2O)_2(l\text{-chxn})_2]X_2$: $X = Cl^-$, Br^- or NO_3^-). The bromide and nitrate underwent deaquation-anation accompanied by a trans to cis configurational change upon heating, converting to *cis*-dibromo or *cis*-nitrato species. Only the chloride showed a simple deaquation-anation, retaining the original trans configuration. These results were obviously different from those of the corresponding complexes with the racemate (*dl*-chxn).

INTRODUCTION

We have studied the thermal reactions of nickel(II) complexes containing C- or N-substituted ethylenediamines, $[Ni(diamine)_2]X_2$ or $[Ni(H_2O)_2(diamine)_2]X_2$ ($X = Cl^-$, Br^-, I^-, NO_3^- or ClO_4^-), in the solid state, and the effects of the C- or N-substituent(s) on the reaction patterns [1,2]. In the course of these studies, we have also reported that several complexes with C-substituted ethylenediamines undergo reversible structural isomerization from square planar to octahedral based on thermal anation [2]. This type of structural 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 (approx. 3.0 BM). Whether the isomerization occurs depends strongly upon the steric effects of the C-substituent(s) on the diamine; among four types of diamines (mono-substituted, the *dl*- or

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meso form of 1,2-di-substituted, and 1,1-di-substituted ethylenediamines), the *dl* form diamines, such as *dl*-2,3-butanediamine [3], *dl*-1,2-diphenyl-1,2-ethanediamine [4], and *dl*-1,2-cyclohexanediamine [2] were most suitable for the isomerization. Our previous report [2] discussed the substituent effects of the four kinds of diamines on the thermal reactions. In the present study, in order to examine the effects in further detail, the thermal reactions of the complexes containing optically active 1,2-cyclohexanediamine (*l*-chxn) were investigated and the results were compared with those of the corresponding complexes with the racemate (*dl*-chxn) which undergo square planar to octahedral structural isomerization in the case of the chloride and bromide [2].

EXPERIMENTAL

Materials

The ligand, *l*-1,2-cyclohexanediamine (*l*-chxn) was resolved from the racemate [5] by the known method [6]. The complexes were prepared by the following method. To an ethanolic solution of a nickel(II) salt, $NiX_2 \cdot nH_2O$ ($X = Cl^-$, Br^- or NO_3^-), a suspension of the ligand in ethanol and diethyl ether was added dropwise in the molar ratio of 1:2. After stirring for several hours, the residue was removed and the filtrate was 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 then diethyl ether.

The thermal reaction products were obtained on isothermal heating of the starting complexes at their formation temperatures (which were inferred from the results of the thermal analysis) in an electric furnace under static air. They were studied directly after preparation, or in a thoroughly dried atmosphere, to avoid the occurrence of back reactions to the original complexes.

Measurements

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 Jasco UVIDEC-410 spectrophotometer equipped with a reflection attachment. For the spectra in the near-IR region, a Hitachi 340 spectrophotometer was used. IR spectra were recorded with a Jasco IR-A3 spectrophotometer in Nujol mulls.

RESULTS AND DISCUSSION

Structures of the original complexes

The analytical data (not shown) suggest that all the complexes prepared are of the composition, $NiX_2(l\text{-chxn})_2(H_2O)_2$. The electronic spectra of the complexes are shown in Fig. 1. The number of observed bands and their modes of splitting clearly indicate that the original complexes have trans octahedral structures [7]. In addition, the fact that the peak maxima of the complexes are nearly unchanged irrespective of the X^- ion, yields the formula *trans*-$[Ni(H_2O)_2(l\text{-chxn})_2]X_2$ ($X = Cl^-$, Br^- or NO_3^-).

Thermal analyses

Figure 2 shows the results of simultaneous TG–DTA and DSC analyses for all the complexes. The abrupt weight loss observed in each TG curve below 100°C and the corresponding endothermic DTA peaks are due to the liberation of two moles of coordinated water, which is responsible for the color change from violet to violet-blue. After dehydration, the complexes no longer show changes in the TG and DTA curves, or in their colors, until they are decomposed. The DSC curves of the chloride and bromide, which were scanned using a particularly high sensitivity scale, also give no peaks except for those due to dehydration.

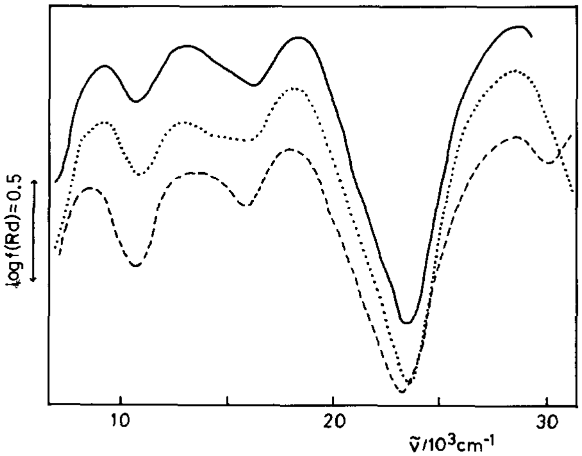


Fig. 1. Electronic spectra of *trans*-$[Ni(H_2O)_2(l\text{-chxn})_2]X_2$, where X is Cl^- (———), Br^- (······) and NO_3^- (– – – –).

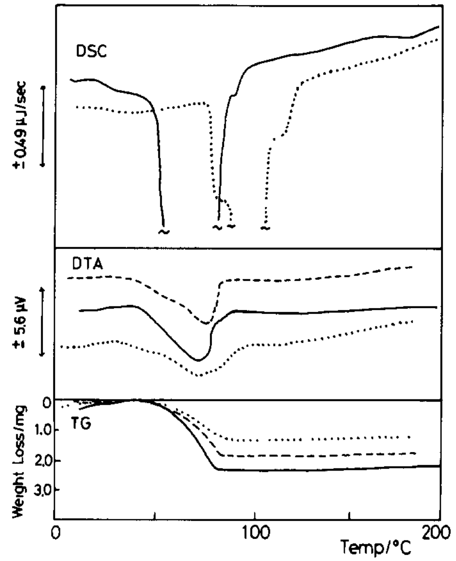


Fig. 2. TG–DTA and DSC results of *trans*-[Ni(H_2O)$_2$(*l*-chxn)$_2$]X_2, where X is Cl^- (———), Br^- (······) and NO_3^- (– – – –), under a constant flow of N_2 at 0.2 dm^3 min^{-1} (heating rate, 2°C min^{-1} for all runs; sample weight, 20.2, 21.0, and 22.6 mg for TG–DTA of the chloride, bromide, and nitrate, and 11.3 and 10.7 mg for DSC of the chloride and bromide).

Spectral changes of the complexes upon heating

Figure 3 shows the electronic spectra of the anhydrous products. The spectral pattern of the chloride remains nearly unchanged after dehydra-

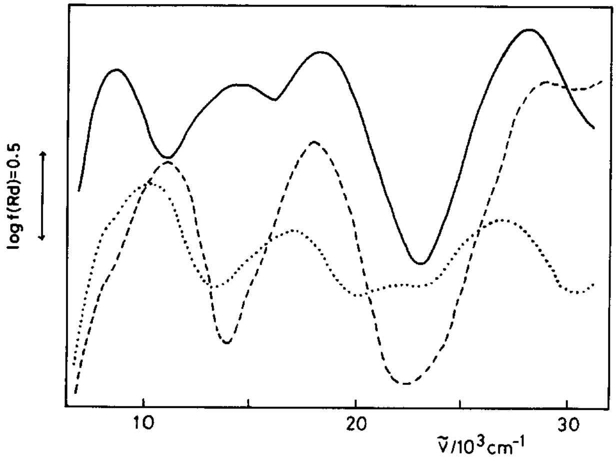
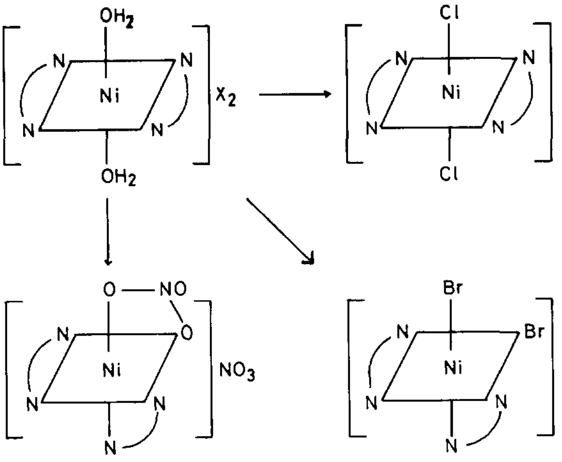


Fig. 3. Electronic spectra of the anhydrous products, NiX_2(*l*-chxn)$_2$, where X is Cl^- (———), Br^- (······), and NO_3^- (– – – –).



Scheme 1.

tion, suggesting that the trans octahedral configuration is retained. Slight shifts of the bands indicate a partial exchange of the axial ligands ($H_2O \rightarrow Cl^-$). However, the bromide and nitrate complexes give different spectral patterns after dehydration compared with those of the original trans complexes. The configurations of these products are cis, because their d–d bands in the near-IR region scarcely show any splitting, to give apparently only one peak [7,8].

The coordination mode of the nitrate ion was also determined by IR spectrophotometry of the nitrate. It is well known that, in general, a NO_3^- ion in a metal complex gives rise to a weak combination band in the region of 1800–1700 cm^{-1} [9]. In the present case, the diaqua complex shows a single peak at 1768 cm^{-1} assignable to the free NO_3^- ions. This peak splits into three peaks at 1730, 1745 and 1756 cm^{-1} in the spectrum of the anhydrous product. This suggests that the product contains free and bidentate NO_3^- ions simultaneously [9].

The thermochemical changes of the complexes observed can thus be represented by Scheme 1. The bromide and nitrate undergo deaquation-anation accompanied by a trans-to-cis configurational change, while the chloride shows a simple deaquation-anation, retaining the original trans configuration.

Comparison with the thermal reactions of dl-*chxn complexes*

The thermal reaction patterns of the *l*-chxn complexes clarified in this work are compared with those of the corresponding complexes containing the racemate (*dl*-chxn) in Table 1. Oh and Oh′ in the table represent octahedral structures containing water molecules and anion(s) as ligand

TABLE 1

Thermal reaction patterns of 1,2-cyclohexanediamine complexes

X	*l*-chxn	*dl*-chxn
Cl^-	Oh → Oh′	Oh → Sp → Oh′
Br^-	Oh → Oh′*	Oh → Sp → Oh′
NO_3^-	Oh → Oh′*	Oh → Oh′

For the definitions of Oh, Oh′ and Sp, see text. Most of the Oh and Oh′ complexes are trans; the cis–octahedral complexes are marked with asterisks.

respectively, while Sp indicates square planar structure. Oh → Sp → Oh′ thus implies that the diaqua octahedral species undergoes deaquation changing into the square planar species, and then transforms into the aniono-octahedral species by anation upon further heating; deaquation-anation takes place in two steps and the latter step corresponds to structural isomerization. The isomerizations of the chloride and bromide occur at 152–173°C and 128–166°C respectively, showing clear endothermic peaks on the respective DTA curves which were measured under the same sensitivity scale as those of the *l*-chxn complexes [2].

Both *l*-chxn and *dl*-chxn produce complexes with the same composition and structure, *trans*-$[Ni(H_2O)_2(diamine)_2]X_2$, as the starting materials of thermal reactions. However, pronounced differences were observed between the thermal reactions of these two diamine complexes. When *dl*-chxn was replaced by *l*-chxn in the complexes, structural isomerization of Sp → Oh′ was no longer observed. In addition, cis configuration is favored in the reaction products of *l*-chxn complexes; the bromide and nitrate undergo deaquation-anation accompanied by a trans-to-cis configurational change.

What is the reason for these differences? It is known that the *dl*-chxn complexes crystallize as *trans*-$[Ni(H_2O)_2$(*d*-chxn)(*l*-chxn)$]X_2$ which accepts preferentially a pair of the *d*- and *l*-form diamines on complexation [10]. Accordingly, the differences in thermal reactions must come from the slight changes in conformation of diamine ligands between *trans*-$[Ni(H_2O)_2$(*l*-chxn)(*l*-chxn)$]X_2$ and *trans*-$[Ni(H_2O)_2$(*d*-chxn)(*l*-chxn)$]X_2$. In both cases, all the cyclohexyl rings are expected to protrude towards an equatorial direction on the chelate plane [10,11], with the result that the former possesses an inversion center, while the latter is characterized by a reflection plane [12]. Unfortunately, it is not clear at present how these conformational differences affect the thermal reactions. However, the conformation of the two diamines in the *dl*-chxn complexes at least stabilizes the tetragonal (square planar or trans octahedral) structure in the thermal reaction products, compared with those in the *l*-chxn complexes.

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