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Solid-phase thermal cis-to-trans isomerization of the nickel(II) complexes containing 1-benzyl-1,2-ethanediamine

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Abstract

The thermal reactions of trans-$[Ni(H_2O)_2(bezen)_2]X_2.nH_2O$ (bezen = 1-benzyl-1,2-ethanediamine; X = Cl^-, Br^- or NO_3^-; $n = 0$ for Cl^- and Br^-, and $n = 1$ for NO_3^-) were investigated by means of TG/DTA, DSC and electronic spectroscopy in the solid phase. All the trans-diaqua complexes brought about a deaquation-anation on heating, transforming into the cis-dichloro, cis-dibromo, and cis-nitrato complexes. The latter two cis complexes irreversibly isomerized to trans ones upon further heating. This type of isomerization is rare and so interesting. The enthalpy change of the exothermic cis-to-trans isomerization was -7.16 and -11.8 kJ mol^{-1} for the bromide and nitrate, respectively. © 1997 Elsevier Science B.V.

Keywords: 1-Benzyl-1,2-ethanediamine; Cis-trans isomer; Nickel(II) complex; Thermal isomerization

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1. Introduction

Many synthetic studies of octahedral diaqua- and dianionobis(diamine)nickel(II) complexes have indicated that the complexes commonly prefer a trans configuration; a cis configuration is found in only a few limited cases [1–3]. In addition, because either a trans or cis configuration is strongly stabilized for a particular combination of ligands, the isolation of both (trans and cis) isomers has not yet been reported.

Chaudhuri et al. have widely studied on the stereochemistry among the solid-phase thermal decomposition of tris- and bis(*N*-substituted ethylenediamine)nickel(II) complexes [4–6]. We have also currently studied on the stereochemistry of many diaquabis(*N*- or *C*-substituted ethylenediamine)nickel(II) complexes and the products of their solid-phase thermal reactions, and the effects of *N*- or *C*-substituent group(s) upon their changes in the coordination structures during thermal treatments [7,8]. We have previously reported that the nickel(II) complexes containing the unsymmetric ethylenediamines such as iso-butanediamine(1,1-dimethyl-1,2-ethanediamine) [9] and *N,N*-dimethylethylenediamine [10] peculiarly provided the instances of a cis configuration among the dianionobis(diamine)nickel(II) complexes obtained by thermal reactions of the corresponding trans-diaqua species. However, systematic knowledge is still lacking for the factors which govern the preference of particular coordination geometries at different temperatures. It looks that, at least, ethylenediamine derivatives with a lower symmetry are more effective for stabilizing a cis geometry.

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In order to examine the effect of a decrease in a symmetry of diamine for the stereochemistry of the complexes, the solid-phase thermochemical changes in the coordination structures of the nickel(II) complexes containing 1-benzyl-1,2-ethanediamine were investigated in the present study. This ligand is an unsymmetrical *C*-mono-substituted ethylenediamine with a considerably bulky substituent so that the anhydrous complexes generated by thermal deaquation-anation would be expected to possess a cis geometry.

2. Experimental

2.1. Materials

The ligand, racemic 1-benzyl-1,2-ethanediamine (bezen) was prepared as follows. Racemic methyl 2-amino-3-phenylpropanoate (DL-phenylalanine methyl ester) was converted into racemic 2-amino-3-phenylpropanamide by the method of Arpesella et al. [11]. Racemic bezen was obtained by reducing the amide with $LiAlH_4$ according to the procedure by Yano et al. [12]. The complexes, trans-$[Ni(H_2O)_2(bezen)_2]X_2.nH_2O$ (where X is Cl^-, Br^- or NO_3^-; *n* is 0 for Cl^- and Br^-, and 1 for NO_3^-), were prepared by the following method. To an aqueous solution of a nickel(II) salt, $NiX_2.nH_2O$ ($X = Cl^-$, Br^- or NO_3^-), a methanolic solution of bezen was added dropwise in the molar ratio of 1 : 1.5. The solutions were allowed to stand for several days in a refrigerator 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, 45.96; H, 6.93; N, 11.80%; calculated for the chloride ($NiC_{18}H_{32}N_4O_2Cl_2$): C, 46.39; H, 6.92; N, 12.02%. Found: C, 38.70; H, 5.67; N, 9.96%; calculated for the bromide ($NiC_{18}H_{32}N_4O_2Br_2$): C, 38.96; H, 5.81; N, 10.10%. Found: C, 39.78; H, 6.14; N, 15.74%; calculated for the nitrate ($NiC_{18}H_{34}N_6O_9$): C, 40.25; H, 6.38; N, 15.64%.

2.2. Measurements

Simultaneous TG-DTA or DSC measurements were carried out with a Seiko SSC/580 TG/DTA-30 or DSC-10 apparatus. Each run was performed under a constant flow of nitrogen (0.2 dm^3 min^{-1}) at a heating rate of 2°C min^{-1}; about 20 mg or 10 mg of sample was used for TG-DTA or DSC, respectively. Electronic spectra in the solid phase were measured by the diffuse reflectance method with a JASCO V-570 UV/VIS/NIR spectrophotometer equipped with a reflection attachment. The spectra at elevated temperatures were monitored by the use of a JASCO heating cell, which was set up on the apparatus and was controlled by a Toho Denshi BX-304 temperature controller equipped with a platinum thermocouple. The measurements were carried out by 10°C from room temperature until decomposition temperature after the sample was heated to the setting temperature and then kept to that temperature for about 30 min. IR spectra were recorded with a HORIBA FT-210 spectrometer by the KBr disk method.

3. Results and discussion

3.1. Thermal analyses

Fig. 1 shows the results of simultaneous TG-DTA for the complexes. The abrupt weight losses observed on the TG curves below 100°C and the corresponding endothermic DTA peaks are due to the liberation of water molecules (% weight losses: obsd., 8.3%; calcd. for the chloride, 7.7%; 6.2% and 6.5% for the bromide; 9.0% and 10.1% for the nitrate). In this dehydration step, the chloride and bromide change their colors from violet to violet-blue, while the nitrate scarcely shows any color change. After the dehydration, a small exothermic peak appears at approx. 130–160°C and 110–120°C for the bromide and nitrate, respectively, while the TG curves remain flat at these temperature ranges. The color of the bromide further converts to blue-violet by this exothermic reaction.

3.2. Electronic spectra

Fig. 2 shows the solid-phase electronic spectra of the chloride at room temperature and at 110°C. The latter corresponds to the violet-blue anhydrous species. The number of observed bands and the mode of splitting clearly indicate that the former has a trans octahedral geometry, while the latter has a cis octahedral one [13]: it is found that trans-$[Ni(H_2O)_2(bezen)_2]Cl_2$ loses the coordinated water molecules to

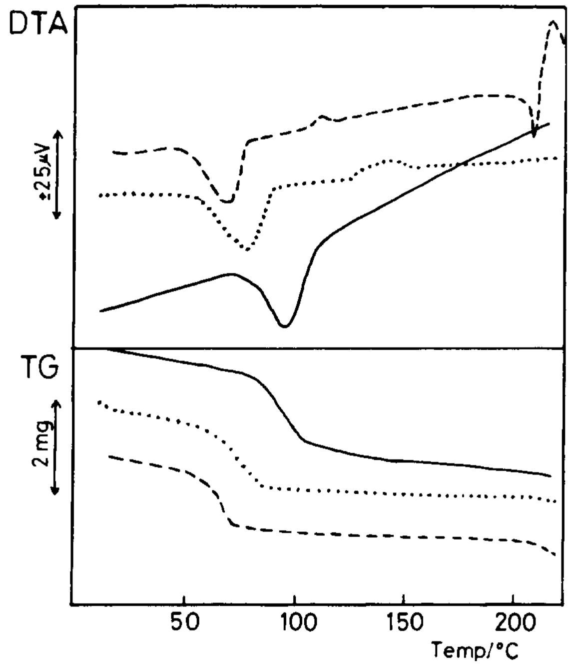

Fig. 1. TG-DTA results for trans-$[Ni(H_2O)_2(bezen)_2X_2.nH_2O$, where X is Cl^- (———), Br^- (···) and NO_3^- (- - -), under a constant flow of N_2 at 0.2 $dm^3\ min^{-1}$ (heating rate, 2°C min^{-1} for all runs; sample weight, 24.3, 26.0, and 19.9 mg for the chloride, bromide and nitrate, respectively).

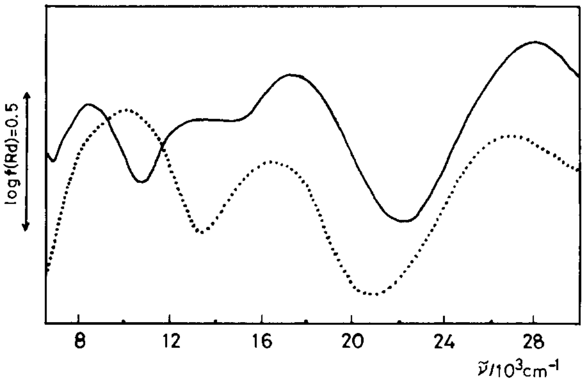

Fig. 2. Electronic spectra of trans-$[Ni(H_2O)_2(bezen)_2]Cl_2$ at room temperature (———) and at 110°C (···).

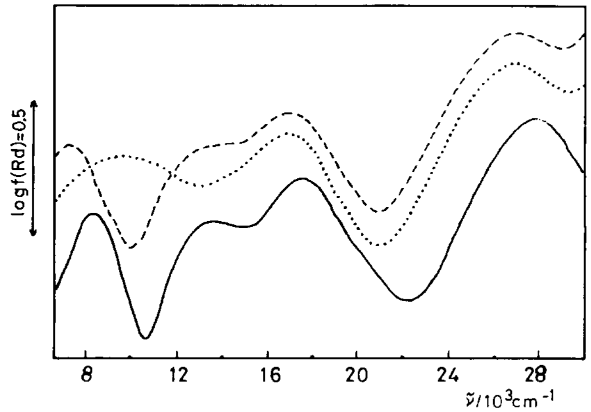

Fig. 3. Electronic spectra of trans-$[Ni(H_2O)_2(bezen)_2]Br_2$ at room temperature (———), at 120°C (···) and at 150°C (- - -).

change into cis-$[NiCl_2(bezen)_2]$ by thermal deaquation-anation.

Fig. 3 shows the electronic spectra of the bromide at room temperature, at 120°C and at 150°C. The blue-violet species at 150°C has a spectral pattern identical with that of the original trans octahedral species (at room temperature) except for a slight shift of the bands, which indicates a partial exchange of the ligands ($H_2O \rightarrow Br^-$). On the other hand, the spectrum of the violet-blue species at 120°C is characteristic of a cis octahedral structure. Thus, the bromide undergoes a deaquation-anation to generate cis-$[NiBr_2(bezen)_2]$ and then the cis complex isomerizes to the trans form upon further heating. It seems that the exothermic peak observed at 130–160°C on the DTA is associated with this isomerization.

For the nitrate, a pronounced thermochromism was not observed until the decomposition point. However, the view of the spectral changes upon heating is almost similar to that of the bromide (Fig. 4). The coordination mode of the nitrate ions was also determined by IR spectrometry. 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 1700–1800 cm^{-1} [14]. In the present case, the diaqua complex showed a single peak at 1766 cm^{-1} assignable to the free NO_3^- ions. This peak split into three peaks at 1734, 1762 and 1766 cm^{-1} in the spectrum of the cis octahedral species obtained just after dehydration (at 80°C). This suggests that the complex can be formulated as cis-$[Ni(NO_3)(bezen)_2]NO_3$ possessing both free and bidentate nitrate ions simultaneously [8,14,15]. The cis complex converts into the trans isomer, trans-$[Ni(NO_3)_2(bezen)_2]$ upon further heating (at 110°C). The exothermic peak appearing at 110–120°C on the DTA reflects this isomerization.

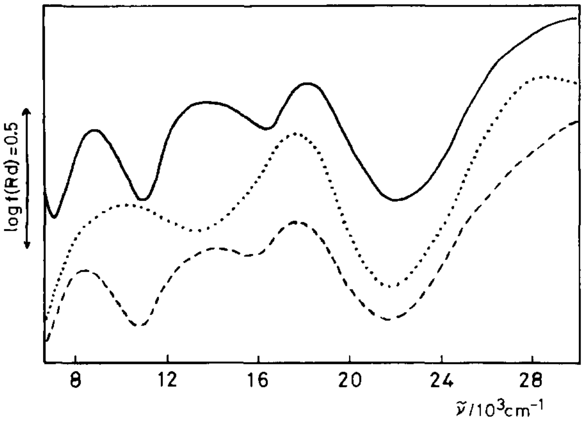

Fig. 4. Electronic spectra of trans-$[Ni(H_2O)_2(bezen)_2](NO_3)_2.H_2O$ at room temperature (———), at 80°C (···) and at 110°C (- - -).

3.3. *Thermal reactions*

The overall reactions of the complexes can thus be represented by the following equations.

$$\text{trans-}[Ni(H_2O)_2(bezen)_2]Cl_2 \rightarrow \text{cis-}[NiCl_2(bezen)_2]$$

$$\text{trans-}[Ni(H_2O)_2(bezen)_2]Br_2 \rightarrow \text{cis-}[NiBr_2(bezen)_2] \rightarrow \text{trans-}[NiBr_2(bezen)_2]$$

$$\text{trans-}[Ni(H_2O)_2(bezen)_2](NO_3)_2 \cdot H_2O \rightarrow \text{cis-}[Ni(NO_3)(bezen)_2]NO_3 \rightarrow \text{trans-}[Ni(NO_3)_2(bezen)_2]$$

The cis-to-trans isomerization was observed in the bromide and the nitrate. This isomerization proceeds exothermically and is irreversible. The enthalpy change of it, which was estimated from the DSC measurement, was -7.16 and $-11.8\,\text{kJ mol}^{-1}$ for the bromide and nitrate, respectively. These values are parallel to, or slightly lower than those of the thermal cis-to-trans or trans-to-cis isomerization taking place in the corresponding chromium(III) complexes, $[CrX_2(diamine)_2]X$ ($X = Cl^-$ or Br^-) [16].

The thermal reaction patterns of the bezen complexes differ from those of the corresponding *C*-monosubstituted ethylenediamine nickel(II) complexes; 1,2-propanediamine, 1,2-butanediamine [17], and 1-phenyl-1,2-ethanediamine [9] provided only the trans anhydrous complexes upon thermal deaquation-anation and showed no such isomerization upon further heating. For the present, only bezen was effective for reducing the energy difference between a cis and trans isomer in this type of complexes. The fact is interesting, but the reasons for it are not clear at present. It is probable however, that the bulkiness of the *C*-substituent group (benzyl group) must be an important factor for such speciality of the bezen complexes.

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