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Thermal Cis-to-Trans Isomerization of $[CoX_2en_2]X$ (X=Cl, Br)

Ryokichi Tsuchiya,* Akira Uehara, and Yoshinori Muramatsu
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

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By measuring calorimetrically the heats of reaction of solid *cis*- and *trans*-$[CoX_2en_2]X$ (X=Cl, Br) with alkaline sodium sulfide solution, the heats of isomerization were obtained as -11.4 kJ mol^{-1} for *cis*-$[CoCl_2en_2]Cl(s)$= *trans*-$[CoCl_2en_2]Cl(s)$ and -6.4 kJ mol^{-1} for *cis*-$[CoBr_2en_2]Br(s)$=*trans*-$[CoBr_2en_2]Br(s)$. Assuming the entropy changes from cis- to trans-form, ΔS, to be -0.0116 kJ mol^{-1} K^{-1} at 25 °C statistically, the free energy changes were calculated as $\Delta G°=-8.0$ kJ mol^{-1} and -3.0 kJ mol^{-1} for the isomerization of *cis*-$[CoCl_2en_2]Cl$ and *cis*-$[CoBr_2en_2]Br$ respectively. From these thermodynamic data, cis-to-trans isomerization was expected to occur in $[CoX_2en_2]X$ (X=Cl or Br), which was verified experimentally by thin-layer chromatography and the spectral measurement.

The cis-to-trans isomerization of $[M^{III}X_2(AA)_2]X$-type chromium complexes in a solid phase has extensively been investigated, where X is a chloride or a bromide ion and AA is a diamine.[1–5] However, the isomerization of the corresponding cobalt(III) complexes has never been studied so widely, because they are often apt to undergo reduction of the metal ion upon heating in a solid phase. The samples of the cobalt(III) complexes so far studied are: Trans-to-cis isomerization for $[CoCl_2(NH_3)_4]IO_3\cdot 2H_2O$,[6] $[CoCl_2pn_2](H_5O_2)Cl_2$,[7] and $[CoBr_2pn_2](H_5O_2)Br_2$;[8] cis,trans(Cl,Cl)-to-cis,cis isomerization for $[CoCl_2(NH_3)_2en]ClO_4$[9] and $[CoCl_2(NH_3)_2en]Br\cdot H_2O$.[10] On the other hand, for $[CoCl_2en_2](H_5O_2)Cl_2$ and $[CoBr_2en_2](H_5O_2)B_2$, neither trans-to-cis nor cis-to-trans isomerization has been found in a solid phase.

The present study was undertaken 1) to find whether or not the isomerization can occur in a solid phase from the viewpoint of enthalpy or free energy changes and, if it does occur, 2) to verify it experimentally.

Experimental

Preparation of Complexes. *trans*-$[CoCl_2en_2]Cl$,[11] *cis*-$[CoCl_2en_2]Cl$,[12] *trans*-$[CoBr_2en_2]Br$,[13] and *cis*-$[CoBr_2en_2]Br$[14] were prepared by the known methods and identified by the elemental analysis and the electronic spectral measurements.

Calorimetric Measurements. The enthalpy changes in the reaction of the trans and cis complexes in the powder state with an alkaline solution of sodium sulfide were measured with a Tokyo-Riko twin isoperibol calorimeter TIC-2S at 25 °C. In each run, the diamine complexes employed were accurately weighed in the range of order of 2×10^{-4} mol and the reacting solution used was 100 cm^3 of 2×10^{-2} mol dm^{-3} of Na_2S in 1 mol dm^{-3} NaOH solution.

Derivatography. The differential thermal analysis (DTA) of the cis complexes was measured with a Derivatograph Typ-OD-102.

Thin Layer Chromatography (TLC). The TLC was employed to distinguish the cis and trans complexes and to confirm the occurrence of isomerization. The TLC plates used were those of silica gel 60F-254 made by Merck Ltd. The developer used was a mixture of *n*-BuOH: H_2O: AcOH=7:2:1.

Electronic Spectra. Electronic spectra of the complexes were recorded on a JASCO Uvidec 550 spectrophotometer.

Results and Discussion

Enthalpy and Free Energy Changes in the Isomerization. The enthalpy changes for the reaction of *cis*- and *trans*-dichloribis(ethylenediamine)cobalt(III) chloride and dibromobis(ethylenediamine)cobalt(III) bromide with sodium sulfide solution were measured as below.

$$\begin{aligned} &\textit{cis}\text{-}[CoCl_2en_2]Cl(s) + {}^3/_2S^{2-}(aq) \\ &\quad = {}^1/_2Co_2S_3(s) + 3Cl^-(aq) + 2en(aq) \\ &\qquad \Delta H = -71.9\ \text{kJ mol}^{-1} \end{aligned} \tag{1}$$

$$\begin{aligned} &\textit{trans}\text{-}[CoCl_2en_2]Cl(s) + {}^3/_2S^{2-}(aq) \\ &\quad = {}^1/_2Co_2S_3(s) + 3Cl^-(aq) + 2en(aq) \\ &\qquad \Delta H = -60.5\ \text{kJ mol}^{-1} \end{aligned} \tag{2}$$

$$\begin{aligned} &\textit{cis}\text{-}[CoBr_2en_2]Br(s) + {}^3/_2S^{2-}(aq) \\ &\quad = {}^1/_2Co_2S_3(s) + 3Br^-(aq) + 2en(aq) \\ &\qquad \Delta H = -46.9\ \text{kJ mol}^{-1} \end{aligned} \tag{3}$$

$$\begin{aligned} &\textit{trans}\text{-}[CoBr_2en_2]Br(s) + {}^3/_2S^{2-}(aq) \\ &\quad = {}^1/_2Co_2S_3(s) + 3Br^-(aq) + 2en(aq) \\ &\qquad \Delta H = -40.5\ \text{kJ mol}^{-1} \end{aligned} \tag{4}$$

By combining Eq. 1 with 2, and Eq. 3 with 4, the enthalpy changes of the isomerization for the dichloro- and dibromo-complexes are obtained as follows:

$$\begin{aligned} &\textit{cis}\text{-}[CoCl_2en_2]Cl(s) = \textit{trans}\text{-}[CoCl_2en_2]Cl(s) \\ &\qquad \Delta H = -11.4\ \text{kJ mol}^{-1} \\ &\textit{cis}\text{-}[CoBr_2en_2]Br(s) = \textit{trans}\text{-}[CoBr_2en_2]Br(s) \\ &\qquad \Delta H = -6.4\ \text{kJ mol}^{-1} \end{aligned}$$

Statistically, the probability of the formation of the cis complex is 4, whereas that of the trans complex is just one, and thereby the entropy of the cis complex is larger than that of the trans one by the value

$$\Delta S = R\ln 4 = 11.5\ \text{J mol}^{-1}\,\text{K}^{-1}.$$

The entropy change of cis-to-trans isomerization is, therefore, $\Delta S=-11.5$ J mol^{-1}K^{-1}, and the free energy changes are calculated as:

$$\begin{aligned} &\textit{cis}\text{-}[CoCl_2en_2]Cl(s) = \textit{trans}\text{-}[CoCl_2en_2]Cl(s) \\ &\qquad \Delta G° = -8.0\ \text{kJ mol}^{-1} \\ &\textit{cis}\text{-}[CoBr_2en_2]Br(s) = \textit{trans}\text{-}[CoBr_2en_2]Br(s) \\ &\qquad \Delta G° = -3.0\ \text{kJ mol}^{-1}. \end{aligned}$$

On the basis of the above data of enthalpy and free

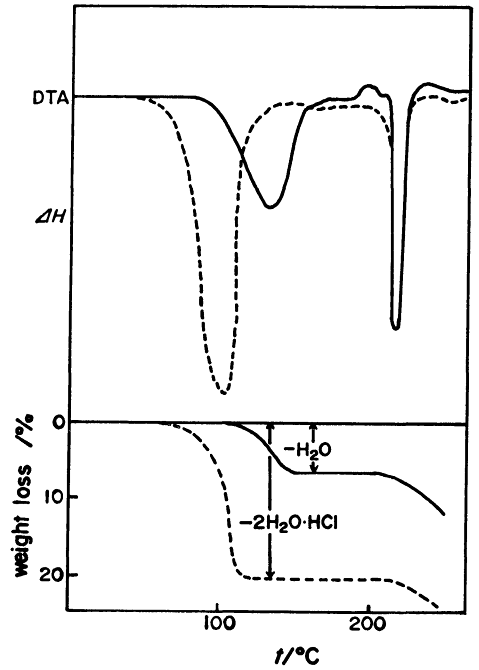

Fig. 1. Derivatograms of *cis*-$[CoCl_2en_2]Cl\cdot H_2O$ (——) and *trans*-$[CoCl_2en_2](H_5O_2)Cl_2$ (------).

Table 1. The results of TLC

Materials	R_f values
Thermal products from *cis*-$[CoCl_2en_2]Cl$	0.56 (blue) 0.24 (green) 0.15 (blue) 0.04(brown)
trans-$[CoCl_2en_2]Cl$	0.24 (green)
cis-$[CoCl_2en_2]Cl$	0.17 (violet)
$CoCl_2\cdot 6H_2O$	0.57 (blue) 0.26 (blue) 0.10 (blue)
Thermal product from *cis*-$[CoBr_2en_2]Br$	0.36
trans-$[CoBr_2en_2]Br$	0.35
cis-$[CoBr_2en_2]Br$	0.30

energy changes, the cis-to-trans isomerization is expected to take place both in $[CoCl_2en_2]Cl(s)$ and $[CoBr_2en_2]Br(s)$, although neither cis-to-trans nor trans-to-cis isomerization has been found for these complexes in a solid phase.

Derivatogtaphy. Figure 1 shows the derivatograms of *cis*-$[CoCl_2en_2]Cl\cdot H_2O$ and *trans*-$[CoCl_2en_2](H_5O_2)Cl_2$. In the latter, neither endo- nor exothermic peak appears, except for the endothermic peaks due to the dehydration plus dehydrochlorination and the decomposition or melting. On the other hand, in the former, in addition to the endothermic peaks due to the dehydration and the decomposition or melting, a small exothermic peak is displayed at *ca.* 200 °C immediately before the decomposition or melting of the complex. In the isothermal heating of *cis*-$[CoCl_2en_2]Cl$ and *cis*-$[CoBr_2en_2]Br$, the color change from violet to green was observed at 215 °C and 210 °C, respectively. Therefore, the appearance of an exothermic peak in the derivatogram of *cis*-$[CoCl_2en_2]Cl$ suggests the occurrence of isomerization to the corresponding trans-form.

TLC. In order to identify the components of thermal products of *cis*-$[CoCl_2en_2]Cl$ and *cis*-$[CoBr_2en_2]Br$, the products were examined by means of TLC. The results of TLC are listed in Table 1. In the dichloro complex, four spots were clearly developed. The R_f value of 0.24 of the green spot is identical with that (0.24) of *trans*-$[CoCl_2en_2]Cl$ freshly prepared, and the value is obviously distinguished from those of the other spots due to the original cis complex and others. The thermal product obtained from *cis*-$[CoBr_2en_2]Br$ gave the R_f value of 0.36, which is also very close to that (0.35) of *trans*-$[CoBr_2en_2]Br$ freshly prepared.

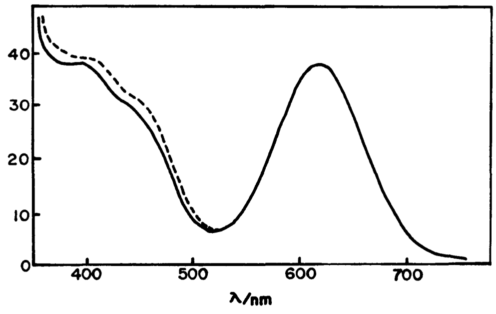

Fig. 2. Electronic spectra of *trans*-$[CoCl_2en_2]Cl$ (——) and of the third fraction of thermal products from *cis*-$[CoCl_2en_2]Cl$ (------).

Spectral Measurements. In order to confirm the formation of *trans*-$[CoX_2en_2]X$ from the thermal reaction of the corresponding cis complexes, the thermal product was separated by means of column chromatography. The thermal product of the cis-dichloro complex was separated into four fractions on a column of the cation exchange resin (SP Sephadex C-25, H^+ form). The third fraction was green and eluted with 0.1 mol dm^{-3} HCl methanolic solution. The green product of the cis-dibromo complex was separated on a column of cellulose and eluted with methanol as rapidly as possible because the trans-dibromo complex is readily isomerizes to the original cis-form during elution. The electronic spectrum of the green compound thus obtained from *cis*-$[CoCl_2en_2]Cl$ is shown in Fig. 2. It is almost identical with that of *trans*-$[CoCl_2en_2]Cl$ freshly prepared. The same result is obtained for the dibromo complex.

The results of the above experiments support that both *cis*-$[CoCl_2en_2]Cl$ and *cis*-$[CoBr_2en_2]Br$ isomerize to the corresponding trans-form in a solid phase as expected from the thermodynamic consideration.

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