Derivatographic Studies on Transition Metal Complexes. VII.[1] Thermal *cis, trans*-to-*trans, cis* Isomerization of $[CoCl_2(NH_3)_2en]Br \cdot H_2O$ in Solid Phase[2]

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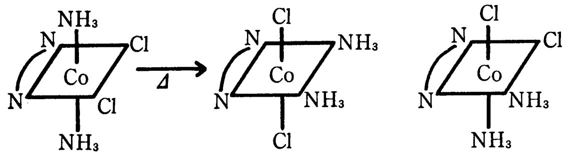
The *cis, trans*-to-*trans, cis* isomerization as well as dehydration of $[CoCl_2(NH_3)_2en]Br \cdot H_2O$ were investigated by using derivatographic, isothermal, and sealed tube methods. Isomerization in a solid phase proceeded regardless of whether its state was monohydrate or anhydride. Two distinct processes were found for isomerization, one being accompanied by the liberation of water of crystallization and the other taking place after complete liberation of water of crystallization. Both reactions were of the first order. The thermochemical functions were obtained to be $\Delta H=(12\pm2)$ kcal/mol, $E^{\neq}=(28\pm3)$ kcal/mol and $\Delta S^{\neq}=(-10\pm4)$ e.u. for dehydration. The values $E^{\neq}=(28\pm3)$ kcal/mol and $S^{\neq}(-4\pm2)$ e.u. were estimated for isomerization in the first process, and $E^{\neq}=(28\pm3)$ kcal/mol and $\Delta S^{\neq}=(-12\pm3)$ e.u. for that in the second process. As a possible reaction mechanism for isomerization, an "aquation-anation mechanism" was introduced for the first process and an "intramolecular mechanism" for the second.

It is known that, owing to the small energy change in isomerization, some cis-complexes turn into the corresponding trans-complexes[3] and other trans-complexes are converted into the cis-complexes[4–7] in a solid phase. A striking feature particularly of isomerization in a solid phase is that the reactions are sensitively affected by the kind of counter ionic species contained, in contrast to the reactions in aqueous solution. As an example, the variation of the counter ion X in *cis, trans*-$[CoCl_2(NH_3)_2en]X$ type gives rise to a different reaction upon heating in a solid phase. In the case of X=Cl, no isomerization could be observed, whereas in the case of $X=ClO_4$, isomerization into the corresponding *trans, cis*-form[3] took place and in the case of X=SCN, the *cis, trans*-complex was converted into *cis, cis*-$[CoCl(NCS)(NH_3)_2en]Cl$.[1]

It is of interest to investigate the cause of isomerization path-ways differing with the kind of counter ionic species. For studying the problem, we attempted to observe the isomerization of *cis, trans*-$[CoCl_2(NH_3)_2en]Br \cdot H_2O$ and its anhydride as one of the series of studies on *cis, trans*-$[CoCl_2(NH_3)_2en]X$ type complexes. Three geometrical isomers of $[CoCl_2(NH_3)_2en]^+$ are schematically drawn in Fig. 1, together with their colors. When the monohydrate and anhydride of the corresponding bromide are heated in a solid phase, a distinct color change from blue to green is observed. This thermal isomerization step is shown by an arrow in Fig. 1. This paper deals with the measurement of rate and the estimation of the kinetics of isomerization as well as dehydration in the complex bromide.



cis, trans-form (blue)   *trans, cis*-form (green)   *cis, cis*-form (violet)

Fig. 1. Geometrical isomers of $[CoCl_2(NH_3)_2en]^+$.

Experimental

Preparation of Complexes. The complex, *cis,trans*-$[CoCl_2(NH_3)_2en]Br \cdot H_2O$ was prepared by the method of Bailar and Pepard.[8] The corresponding bromide was obtained by saturating the solution of the chloride with ammonium bromide at room temperature and by standing it in a refrigerator for a while. Purification was achieved by recrystallization from water. Blue crystals deposited out were filtered, washed with a small amount of cold water, ethanol and ether, and air-dried.

Found: C, 7.46; H, 5.00 N, 17.29%. Calcd for *cis,trans*-$[CoCl_2(NH_3)_2en]Br \cdot H_2O$: C, 7.46; H, 4.95; N, 17.39%.

The complex *trans,cis*-$[CoCl_2(NH_3)_2en]Cl$ was also prepared by the method of Bailar and Pepard for the corresponding *cis,trans*-complex.

Derivatographic Measurement. The apparatus and techniques for derivatography used were the same as described previously.[9]

Isothermal Measurement. A Shimadzu TM-1A Thermano balance and Abderhalden apparatus were used for the isothermal measurment. The measurement and analytical method were also the same as given previously.[9] In order to determine the ratio of the two isomers in the sample in each heating step, the visible and UV absorption spectra of the complexes were measured with a Hitachi R-3 Spectrophotometer. The electronic spectra of the complexes in DMF-water mixture (4 : 1), *cis, trans*-$[CoCl_2(NH_3)_2en]Br \cdot H_2O$, *trans,cis*-$[CoCl_2(NH_3)_2en]Br$ and the reaction product obtained by heating the former are given in Fig. 2. Since *cis,trans*- and *trans,cis*-complexes exhibit the absorption coefficients 110 and 34 at 598 nm ($\nu=50.17\times10^{13}\ sec^{-1}$) and 92 and 41 at 625 nm ($\nu=48.00\times10^{13}\ sec^{-1}$), respectively,

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[1] Part VI, R. Tsuchiya, M. Suzuki, and E. Kyuno, This Bulletin, **44**, 709 (1971).

[2] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[3] R. Tsuchiya, A. Nakata, and E. Kyuno, This Bulletin, **44**, 705 (1971).

[4] H. E. LeMay, Jr., and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 5577 (1967).

[5] R. Tsuchiya, K. Murai, and E. Kyuno, This Bulletin, **43**, 1383 (1970).

[6] R. Tsuchiya, Y. Kaji, and E. Kyuno, *ibid.*, **43**, 1906 (1970).

[7] N. I. Lobanov, *Zhur. Neorg. Khim.*, **4**, 151 (1959).

[8] J. C. Bailar, Jr., and F. Pepard, *J. Amer. Chem. Soc.*, **62**, 105 (1940).

[9] R. Tsuchiya, Y. Kaji, and E. Kyuno, This Bulletin, **42**, 1881 (1969).

the ratios *cis, trans*/*trans, cis* of two isomers in each product were determined spectrophotometrically by means of the following equations,

$$\left.\begin{aligned}110X+34Y&=D_{598}\\ 92X+41Y&=D_{625}\end{aligned}\right\}\tag{1}$$

where X and Y are the concentrations (mol l^{-1}) of *cis, trans*-complex and *trans, cis*-complex, respecitvely, and D_{598} and D_{625} are the observed absorbancies at 598 nm and 625 nm, respectively, with 1.0 cm cell.

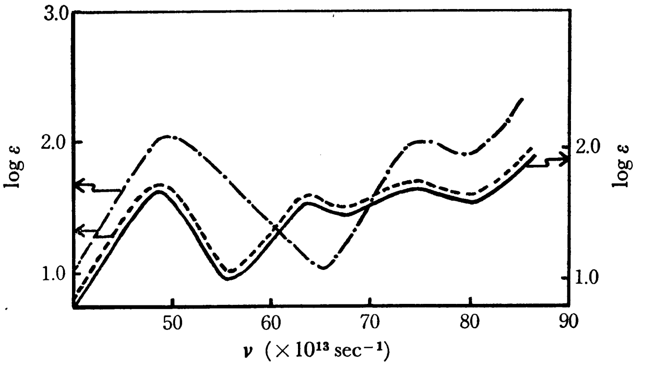

Fig. 2. Electronic spectra of *cis, trans*-[$CoCl_2(NH_3)_2en$]Br·H_2O (——), *trans, cis*-[$CoCl_2(NH_3)_2en$]Br (——), and the product obtained by heating the former (----).

IR Spectral Measurement. The IR and Far IR spectra were measured by a nujol-mull method using JASCO Model IR-E and IR-F Spectrophotometers both in NaCl and in CsBr regions.

Results and Discussion

Structural Assignment. IR spectra of the complexes are shown in Fig. 3. In order to determine the geometric configuration in the thermal reaction product of *cis, trans*-[$CoCl_2(NH_3)_2en$]Br·H_2O, δ_{NH_2} bands appearing in 1250—1350 cm^{-1},[1,10] ν_{Co-N} bands in 450—550 cm^{-1},[12] and ν_{Co-Cl} bands in 300—360 cm^{-1},[11] should be carefully studied.

The three wave number regions where the absorption peaks appear differ to some extent in *cis, trans*-[$CoCl_2(NH_3)en$]Br·H_2O and *trans, cis*-[$CoCl_2(NH_3)en$]Br as seen in Fig. 3. On the other hand, the absorption peaks for δ_{NH_2}, ν_{Co-N} and ν_{Co-Cl} in the thermal reaction product were found to be in fair agreement with those in *trans, cis*-[$CoCl_2(NH_3)_2en$]Br.

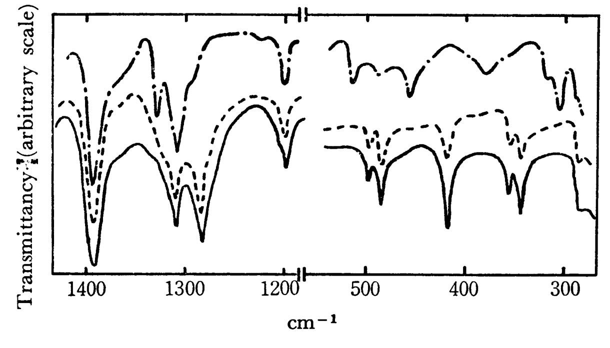

Fig. 3. IR spectra of *cis, trans*-[$CoCl_2(NH_3)_2en$]Br·H_2O (——), *trans, cis*-[$CoCl_2(NH_3)_2en$]Br, (——), and the product obtained by heating the former (----).

If the thermal exchange between chloride ion coordinating to the central metal ion and bromide ion in the outer coordination sphere occurs in the isomerization process, the bands in 300—360 cm^{-1} for the reaction rpoduct should differ from those for *trans, cis*-[$CoCl_2(NH_3)_2en$]Br. A similar exchange has been found in the isomerization, *cis, trans*-[$CoCl_2(NH_3)_2en$]SCN·H_2O ⟶ *cis, cis*-[$CoCl(NCS)(NH_3)_2en$]Cl.[1] However, no such exchange could be observed in *cis, trans*-[$CoCl_2(NH_3)_2en$]Br·H_2O.

Thus, it is concluded that the thermal reaction product of *cis, trans*-[$CoCl_2(NH_3)_2en$]Br·H_2O is *trans, cis*-[$CoCl_2(NH_3)_2en$]Br.

Derivatography. The derivatogram for *cis, trans*-[$CoCl_2(NH_3)_2ne$]Br·H_2O, is shown in Fig. 4, where the heating rate applied is 1°/min. The TG curve indicates that dehydration begins at about 90°C and is complete at 125°C and no further loss of weight is detectable until about 150°C. The DTA curve exhibits two overlapped, broad endothermic peaks: the first endothermic peak is centered at 100°C corresponding to genuine dehydration, and is followed by the second, somewhat less intense peak at 120—125°C, corresponding to the dehydration accompanied by the partial isomerization. Other endothermic and exothermic peaks appear at 150—170°C suggesting further decomposition from the TG curve. The DTG curve exhibits similar peaks to those in the DTA curve.

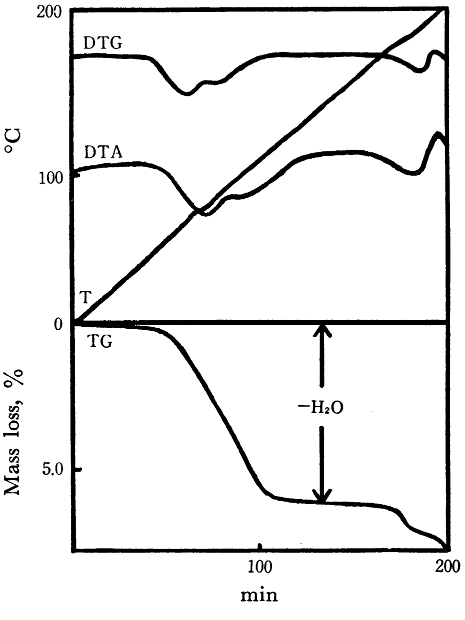

Fig. 4. Derivatogram for *cis, trans*-[$CoCl_2(NH_3)_2en$]Br·H_2O.

The enthalpy change ΔH in the genuine dehydration was estimated to be (12±2) kcal/mol by means of analysis of the first endothermic peak.[9] The value is comparable to the enthalpy change in the dehydration from the general hydrate.

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[10] For *cis, trans-* and *trans, cis*-[$CoCl_2(NH_3)_2en$]Cl: E. Kyuno, *Nippon Kagaku Zasshi*, **80**, 722 (1959).

[11] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

Rate Law for Dehydration and Isomerization. From the measurement of the weight change with a thermobalance at several isothermal temperatures in the region 100—140°C, the relationship between mass loss and time was obtained. By measurement of the absorption of the samples picked up at desired time intervals upon heating and application of equations (1), the conversion ratios of *cis, trans* type complexes to *trans, cis* type complexes were calculated. The results are summarized in Table 1.

TABLE 1. THE RATE CONSTANT OF DEHYDRATION k_d, FIRST STEP ISOMERIZATION $k_i{}^*$ AND SECOND STEP ISOMERIZATION $k_i{}^{**}$, AND THERMOCHEMICAL FUNCTIONS

°C	k_d (sec^{-1})	$k_i{}^*$ (sec^{-1})	$k_i{}^{**}$ (sec^{-1})
100	$(1.9\pm0.3)\times10^{-4}$	$(1.1\pm0.4)\times10^{-4}$	$(1.1\pm0.3)\times10^{-6}$
110.8	$(4.6\pm0.4)\times10^{-4}$	$(4.1\pm0.4)\times10^{-4}$	$(2.8\pm0.3)\times10^{-4}$
121.8	$(1.2\pm0.3)\times10^{-3}$	$(1.2\pm0.4)\times10^{-3}$	$(9.1\pm0.3)\times10^{-5}$
138.3	$(6.5\pm0.3)\times10^{-3}$	$(7.1\pm0.5)\times10^{-3}$	$(3.3\pm0.3)\times10^{-4}$

$\Delta H=(12\pm2)$kcal/mol
$E^{\ddagger}=(28\pm3)$ kcal/mol $E^{\ddagger}=(28\pm3)$kcal/mol $E^{\ddagger}=(28\pm3)$ kcal/mol
$\Delta S^{\ddagger}=(-10\pm3)$ e.u. $\Delta S^{\ddagger}=(-4\pm2)$ e.u. $\Delta S^{\ddagger}=(-12\pm3)$ e.u.

Let a denote the initial amount of *cis, trans*-complex monohydrate (in case of dehydration) or of its anhydride (in case of isomerization), x denote the amount of anhydride (dehydration) or *trans, cis*-complex (isomerization) produced, and let the values of log $a/(a-x)$ be plotted against time (Fig. 5.). The results give two crossed straight lines at each temperature, indicating that the reactions proceed in the first order.

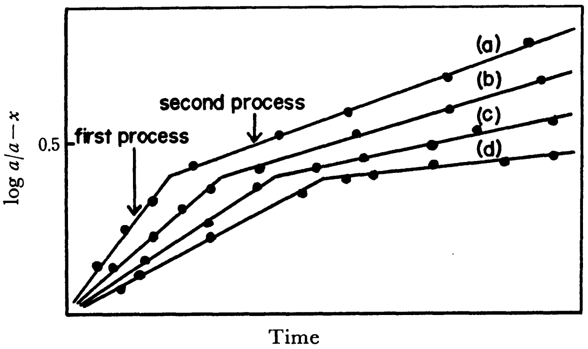

Fig. 5. Plots of log $a/(a-x)$ *vs.* time for isomerization. (a) 138.3°C, (b) 121.8°C, (c) 110.8°C, (d) 100°C Time scales are different in each run.

The appearance of a knick point in each plot suggests the presence of the two steps in isomerization. The first step of isomerization was followed by the dehydration from the complex and *cis, trans/trans, cis* ratios in the product at all temperatures were found to be 40 : 60 at the end of dehydration. The second step of isomerization proceeded in the absence of water.

Rate constants calculated are listed in Table 1, which includes the thermochemical functions estimated from the temperature-dependence of rate constant: the activation energies were obtained from the inclination of the plottings, and the entropies of activation were calculated by means of absolute rate theory.

The thermal reaction schemes are shown in Fig. 6. It is known that the isomerization accompanying dehydration in solid phase was interpreted in terms of the "aquation-anation mechanism," while the isomerization in anhydrous state was explained with the aid of the intramolecular mechanism[12,13]. In the thermal decomposition of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, the above concepts concerning the reaction mechanism were also applied.[5]

It is known that the activation energies in the dehydration and in the isomerization accompanying dehydration are 25—45 kcal/mol[1,5]. A comparison of the above activation energies with that given in Table 1 suggests that the isomerization of *cis, trans*-$[CoCl_2(NH_3)_2en]Br \cdot H_2O$ in solid phase proceeds through "aquation-anation mechanism" in the same way as in aqueous solution.

In order to confirm the presumption, the same thermal isomerization as above was tried in a sealed tube, since isomerization in a sealed tube is expected to be faster than that in an open system. In the anhydrous complex, no further change in reaction rate was found between the sealed tube and the open system. However, the rate of the first step isomerization accompanying dehydration was found to be considerably affected by the vapor pressure from water contained in the complex. This is probably due to the fact that, in the case of anhydride, a small amount of water coexisting with the sample can act only at the surface of solid, while in the hydrated crystals

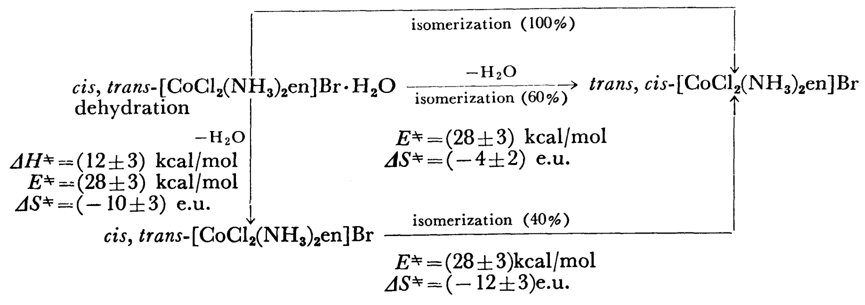

Fig. 6. Thermal reaction schemes.

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12) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958); P. C. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **18**, 289 (1941); **20**, 81 (1943).

13) See for example, F. Basolo, and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed., John Wiley and Sons, Inc., New York, N. Y. (1967), p. 327.

water molecules can easily react with the complex in a sealed tube.

The "aquation-anation" path-way in the isomerization of the *cis, trans*-complex monohydrate to the *trans,cis*-complex monohydrate,

$$\textit{cis, trans}\text{-}[\mathrm{CoCl_2(NH_3)_2en]Br\cdot H_2O} \searrow\!\!\!\rightarrow \textit{trans, cis}\text{-}[\mathrm{CoCl_2(NH_3)_2en]Br} + \mathrm{H_2O}$$

is presumed to consist of the following two steps:

$$\textit{cis, trans}\text{-}[\mathrm{CoCl_2(NH_3)_2en]Br} + \mathrm{H_2O} \searrow\!\!\!\rightarrow \textit{trans, cis}\text{-}[\mathrm{CoCl(H_2O)(NH_3)_2en]BrCl} \quad (\text{or } \textit{cis, trans}\text{-}) \qquad \text{(i)}$$

$$\textit{trans, cis}\text{-}[\mathrm{CoCl(H_2O)(NH_3)_2en]BrCl} \ (\text{or } \textit{cis, trans}\text{-}) \searrow\!\!\!\rightarrow \textit{trans, cis}\text{-}[\mathrm{CoCl_2(NH_3)_2en]Br} + \mathrm{H_2O} \qquad \text{(ii)}$$

Process (ii) may be considered to be the rate determining step since the isomerization was found to proceed according to the first rate law.

On the other hand, it was found that the complex chloride, *cis, trans*-$[CoCl_2(NH_3)_2en]Cl\cdot H_2O$, does not isomerize in the open system but isomerizes in the sealed tube, which gives similar conditions to those in aqueous solution. It may be due to the fact that the water of crystallization has little role in the isomerization of the chloride in the open system.

Since *cis, trans/trans, cis* ratios in the sample obtained immediately after the complete liberation of water of crystallization from *cis, trans*-$[CoCl_2(NH_3)_2en]Br\cdot H_2O$ are independent of the degree of isothermal temperature, a certain amount of water might have no contribution to the isomerization.

The activation energy for the first isomerization, $E^{\neq}=(28\pm3)$ kcal/mol, coincides with that for the dehydration. This suggests that the aquation process (i) is very fast, being followed by the slower anation (ii). Thus the consideration that process (ii) may be the rate determining step is supported and the "aquation-anation mechanism" would be accepted in the isomerization of *cis, trans*-$[CoCl_2(NH_3)_2en]Br\cdot H_2O$.

For the isomerization of anhydrous complex, either of the intramolecular mechanisms, "chain-opening-closing" or "twisting" mechanism, may be considered. If the former is predominant in the isomerization of anhydrous complex, the activation energy would be relatively large owing to the requirement of the bond-breaking energies. The activation energy actually obtained in the second isomerization $E^{\neq}=(28\pm3)$ kcal/mol was, however, considerably smaller than that expected. Thus, "chain-opening-closing" mechanism can be ruled out. On the other hand, "aquation-anation mechanism" also can not be accepted even if the activation energy is eventually equal to that in the first isomerization, since the second isomerization occurs in the absence of water.

Thus, we might conclude that the second isomerization of anhydrous complex *cis, trans*-$[CoCl_2(NH_3)_2en]Br$ proceeds with the aid of "twisting mechanism," because it does not require much activation energy.

With the values of the activation energy $E^{\neq}$ and the entropy of activation $\Delta S^{\neq}$, those of free energy of activation $\Delta G^{\neq}$ were calculated to be 30 kcal/mol and 33 kcal/mol, for the first and second isomerizations respectively. It is obivous from these values that the anhydrous complex is more difficult to isomerize than the hydrate complex.