October, 1972] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3105—3109 (1972) 3105

Derivatographic Studies on Transition Metal Complexes. VIII.[1] Thermal Deaquation-Anation Reaction of *cis*-[CoX(H_2O)N_4]Y_2 Type Complexes in Solid Phase

Ryokichi Tsuchiya, Masatatsu Suzuki,* and Eishin Kyuno
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa
**Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka*

(Received May 15, 1972)

The deaquation-anation reaction of *cis*-[CoX(H_2O)N_4]Y_2 type complexes, where X is chloride or bromide ion, N_4 is tetraammine or bis(ethylenediamine), and Y is chloride, bromide or nitrate ion, was investigated by means of both derivatographic and isothermal methods. Some of these reactions were found to include the stereochemical changes, the structure of reaction products formed by deaquation-anation reaction being considerably affected by the counter ionic species: the chloride complexes, where Y=Cl, were deaquated with retention of *cis*-structure, whereas the bromide complexes, where Y=Br, underwent *cis*-to-*trans* stereochemical change. According to the isothermal measurement in the isomerization of *cis*-[CoCl(H_2O)en_2]$Br_2 \cdot H_2O$, *cis*-[CoCl(H_2O)en_2]Br(NO_3) and *cis*-[CoBr(H_2O)en_2]$Br_2 \cdot H_2O$, these rates were found to obey the first-order rate law and the activation energies, E_a, were obtained to be 38±5, 68±6 and 37±5 kcal mol^{-1} and the enthalpy changes, ΔH, 13.5±2.0, 7.5±2.0 and 13.3±2.0 kcal mol^{-1} for the respective complexes.

Several studies on the thermal deaquation-anation reactions containing the exchange between coordinated water and a counter ion without the displacement of the other ligands in the solid phase are known for [Co(H_2O)$(NH_3)_5$]X_3,[2] [Cr(H_2O)$(NH_3)_5$]X_3,[3] where X is halide, nitrate or sulfate ion, and for *cis*-[CoX(H_2O)en_2]Y_2 type complexes,[4] where X and Y are both halide ions.

In the thermal isomerization reaction, *cis,trans*-[$CoCl_2(NH_3)_2$en]$Br \cdot H_2O$ → *trans,cis*-[$CoCl_2(NH_3)_2$en]Br,[5] *cis*-[CoCl(H_2O)$(NH_3)_2$en]ClBr was presumed to present as an intermediate on the basis of the "aquation-anation" mechanism, the following reaction pathway being deduced,

$$\begin{aligned} &\textit{cis, trans}\text{-}[CoCl_2(NH_3)_2en]Br\cdot H_2O \longrightarrow \\ &\quad \textit{cis}\text{-}[CoCl(H_2O)(NH_3)_2en]ClBr \longrightarrow \\ &\quad \textit{trans, cis}\text{-}[CoCl_2(NH_3)_2en]Br + H_2O. \qquad (1) \end{aligned}$$

Since the stereochemical change is considered to occur in the deaquation-anation of *cis*-[CoCl(H_2O)$(NH_3)_2$en]ClBr in the above pathway (1), it is very interesting to investigate the thermal behavior of halogenoaquo complexes as an intermediate in the isomerization reaction. The aim of this study will be placed on attempting the elucidation of nature for these thermal deaquation-anation reaction involving the stereochemical change and investigating the reaction mechanism thermochemically and kinetically. Such studies on the thermochemical change in the deaquation-anation step will indirectly support the rationality of the reaction pathway (1).

Experimental

Preparation of Complexes. cis-[*CoCl*(H_2O)en_2]$Br \cdot H_2O$: This complex was prepared by the known method,[6] being purified by the recrystallization from a small amount of concentrated hydrobromic acid.

cis-[*CoCl*(H_2O)en_2]*Br*(NO_3). A cold solution of *cis*-[CoCl(H_2O)en_2]$Br_2 \cdot H_2O$ obtained above was treated with saturated solution of lithium nitrate to precipitate the desired reddish violet crystals.

cis-[$CoClBren_2$]$Br \cdot H_2O$ *and* trans-[$CoClBren_2$]NO_3. These compounds were synthesized according to the same method as described in Ref. 6.

cis-[$CoBr_2en_2$]$Br \cdot H_2O$. [Co(CO_3)en_2]Br was treated with alcoholic hydrogen bromide according to the method of Werner[7] to obtain the desired complex.

cis-[*CoBr*(H_2O)en_2]$Br_2 \cdot H_2O$. This compound was prepared by the method of Werner.[7]

cis-[*CoCl*(H_2O)$(NH_3)_4$]Cl_2, cis-[*CoCl*(H_2O)$(NH_3)_4$]Br_2, cis-[*CoBr*(H_2O)$(NH_3)_4$]Br_2 *and* cis-[*CoBr*(H_2O)$(NH_3)_4$]Cl_2: These compounds were synthesized according to the literature.[8]

Derivatographic Measurement. The apparatus and techniques for derivatography used in this work were the same as described in the earlier paper.[3] The heating rate was 1°C min^{-1}.

Isothermal Measurement. A Shimadzu TM-1A Thermanobalance and Abderhalden apparatus were used for the isothermal measurement. The procedure of measurement and analytical method for the experiments are similar to those already described.[9] In order to determine the change of the conversion ratios in the thermal reactions of *cis*-[CoBr(H_2O)en_2]$Br \cdot H_2O$, the visible and UV absorption spectra of the complexes were measured consecutively with a Hitachi R-3 Spectrophotometer with 1.0 cm cell: the ratio of *cis*-[CoBr(H_2O)en_2]$Br \cdot H_2O$, *cis*-[$CoBr_2en_2$]$Br \cdot H_2O$ and *trans*-[$CoBr_2en_2$]Br were estimated by using the following three simultaneous equations,

$$\begin{aligned} 9.5X + 37.0Y + 55.1Z &= D_{530} \\ 85.0X + 111.1Y + 13.4Z &= D_{554} \\ 102.6X + 101.0Y + 14.2Z &= D_{655}, \end{aligned}$$

---

[1] Presented at the 21st Symposium on Coordination Chemistry, Nagoya, October, 1971.

[2] M. Mori, R. Tsuchiya, and Y. Okano, This Bulletin **32**, 1029 (1959).

[3] R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, *ibid.*, **42**, 1881 (1969).

[4] F. C. Chang and W. W. Wendlandt, *Thermochim. Acto*, **1**, 495 (1970).

[5] R. Tsuchiya, M. Suzuki, and E. Kyuno, This Bulletin, **45**, 1065 (1972).

[6] J. W. Vaughn and R. D. Lindholm in S. Y. Tyree, Jr., (ed.) Inorganic Syntheses Vol. IX, McGraw-Hill, New York, 1967, p. 163.

[7] A. Werner, *Ann.*, **386**, 111 (1912).

[8] S. M. Jørgensen, *Z. Anorg. Chem.*, **2**, 294 (1892).

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

TABLE 1. TEMPERATURE RANGE OF DEAQUATION-ANATION AND THE REACTION PRODUCTS

Complex	Temperature range of reaction (°C)	Reaction product
cis-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$	65—130	*cis*- + *trans*-$[CoClBren_2]Br$
cis-$[CoCl(H_2O)en_2]Br(NO_3)$	110—140	*trans*-$[CoClBren_2]NO_3$
cis-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$	70—130	*cis*- + *trans*-$[CoBr_2en_2]Br$
cis-$[CoCl(H_2O)(NH_3)_4]Cl_2$	135—170	*cis*-$[CoCl_2(NH_3)_4]Cl$
cis-$[CoCl(H_2O)(NH_3)_4]Br_2$	100—130	*trans*-$[CoClBr(NH_3)_4]Br$
cis-$[CoBr(H_2O)(NH_3)_4]Br_2$	100—135	*trans*-$[CoBr_2(NH_3)_4]Br$

where X, Y and Z are the respective concentrations (mol l^{-1}) of the above three complexes, and D_{530}, D_{554} and D_{655} are the observed absorbancies at 530 nm, 554 nm and 655 nm, respectively.

Results and Discussion

When a number of aquo complexes of *cis*-$[CoX(H_2O)N_4]Y_2 \cdot nH_2O$ type are heated, the following reaction takes place,

$$cis\text{-}[CoX(H_2O)N_4]Y_2 \cdot nH_2O \longrightarrow cis\text{- or } trans\text{-}[CoXYN_4]Y + (n+1)H_2O.$$

The aquo complexes prepared in the present work listed in Table 1, together with their reaction products and the range of the reaction temperatures.

Derivatography. *(a)* cis-*$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$*: The complex undergoes the following reaction upon heating,

$$cis\text{-}[CoBr(H_2O)en_2]Br_2 \cdot H_2O \longrightarrow cis\text{- + } trans\text{-}[CoBr_2en_2]Br + 2H_2O.$$

The derivatogram for this reaction is shown in Fig. 1, together with those of the other two complexes, *cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$ and *cis*-$[CoCl(H_2O)en_2]Br(NO_3)$, which will be described in the following sections. The TG curve indicates that the liberation of one mole of lattice water and one mole of coordinated water simultaneously begins to appear at about 70°C and ceases completely at 130°C, where the color change from violet to grayish green was observed, and no further mass loss is detected until about 210°C. The DTA curve shows one endothermic peak centered at 80°C, corresponding to the deaquation-anation process, and one more sharp exothermic peak centered at 170°C: in the latter peak region, no change of weight is detected in TG curve.

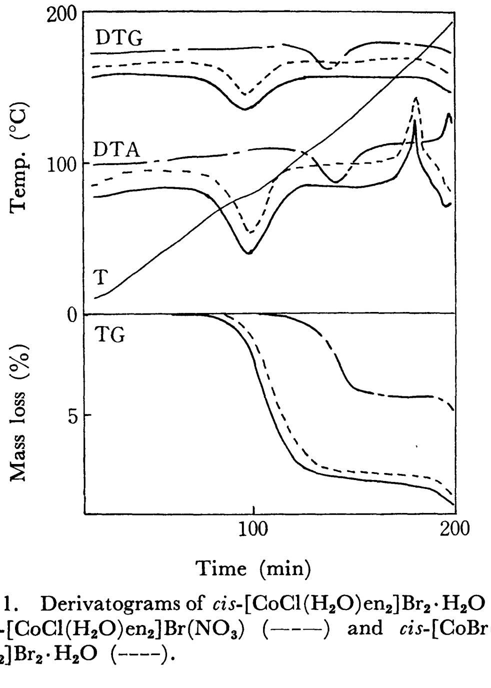

Fig. 1. Derivatograms of *cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$ (——), *cis*-$[CoCl(H_2O)en_2]Br(NO_3)$ (— — —) and *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$ (----).

In order to compare the thermal behavior of halogenoaquo complexes with that of dihalogeno complexes, derivatograms of dihalogeno complexes, *cis*-$[CoBr_2en_2]Br \cdot H_2O$, *cis*-$[CoClBren_2]Br \cdot H_2O$ and *trans*-$[CoBr_2en_2]Br$, are shown in Fig. 2.

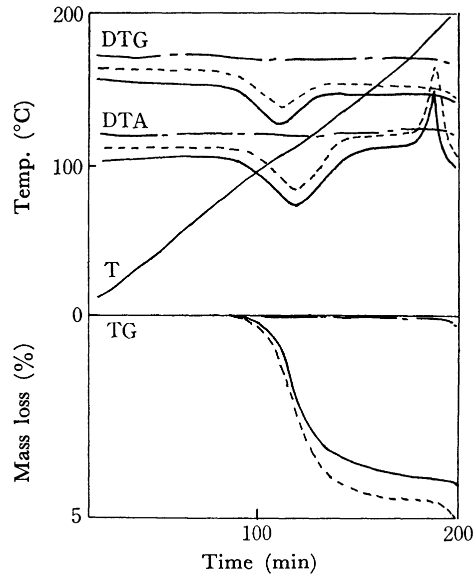

Fig. 2. Derivatograms of *cis*-$[CoBr_2en_2]Br \cdot H_2O$ (——), *cis*-$[CoClBren_2]Br \cdot H_2O$ (----) and *trans*-$[CoBr_2en_2]Br$ (— — —).

When *cis*-$[CoBr_2en_2]Br \cdot H_2O$ was heated, the dehydration reaction began to take place at about 90°C. The TG curve exhibits the mass loss of lattice water in the temperature range of 90 to 160°C and no further mass loss was detected until 210°C. The DTA curve exhibits a large endothermic peak at 120°C and a sharp exothermic peak at 185°C. This curve is approximately the same as that for *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$ in the temperature range of 160 to 210°C. During the dehydration process, the color change from blue to grayish green was observed. This change may be attributed to the *cis*-to-*trans* isomerization,

$$cis\text{-}[CoBr_2en_2]Br \cdot H_2O \rightarrow trans\text{-}[CoBr_2en_2]Br + H_2O.$$

The isomerization could be also interpreted in terms of "aquation-anation" mechanism.[9]

When the trans-complex obtained in the above thermal reaction was cooled to room temperature, the reverse *trans*-to-*cis* isomerization occurred; *i.e.*, the *trans*-complex absorbed one mole of water as shown in the following reaction,

trans-$[CoBr_2en_2]Br + H_2O \rightarrow$ *cis*-$[CoBr_2en_2]Br\cdot H_2O$,

the color change from grayish green to blue being observed.

In the derivatogram of *trans*-$[CoBr_2en_2]Br$ shown in Fig. 2, differing from the corresponding *cis*-complex, no change was found in the DTA curve until the genuine decomposition began to appear at about 210°C. And even when the *trans*-complex was cooled to room temperature after heating, no *trans*-to-*cis* isomerization was observed.

(b) cis-$[CoCl(H_2O)en_2]Br_2\cdot H_2O$*:* The complex undergoes the following reaction upon heating,

cis-$[CoCl(H_2O)en_2]Br_2\cdot H_2O$

$\longrightarrow$ *cis*- + *trans*-$[CoClBren_2]Br + H_2O$.

The derivatogram for this change is very similar to that for the corresponding bromoaquo-bromide (a) as shown in Fig. 1. The TG curve indicates that the mass loss of lattice water begins to appear at approximately 65°C. An endothermic peak is observed at 85°C in the DTA. The deaquation-anation was completed at 130°C, and the mass was kept constant until 180°C, whereupon the genuine decomposition began to occur as shown in the TG curve. The DTA curve exhibits a sharp exothermic peak at a similar temperature, 175°C, to that seen in the corresponding bromoaquo-bromide complex.

The sharp exothermic peak is also found or *cis*-$[CoClBren_2]Br\cdot H_2O$ at the same temperature as shown in Fig. 2. The thermochromism was also observed in the dehydration process,

cis-$[CoClBren_2]Br\cdot H_2O \rightarrow$ *trans*-$[CoClBren_2]Br + H_2O$,

in the temperature range of 95 to 155°C. The *trans*-complex obtained above was hygroscopic and completely turned back to *cis*-complex again under cooling.

(c) cis-$[CoCl(H_2O)en_2]Br(NO_3)$*:* The complex undergoes the following reaction upon heating at 110—140°C, *cis*-$[CoCl(H_2O)en_2]Br(NO_3) \rightarrow$ *trans*-$[CoClBren_2]NO_3+H_2O$, as shown in Fig. 1, the color change from violet to green being found. The DTA curve exhibits an endothermic peak at 130°C and an exothermic peak at 200°C, which correspond to the deaquation-anation and the genuine decomposition reactions respectively.

(d) cis-$[CoCl(H_2O)(NH_3)_4]Cl_2$*:* The derivatogram of *cis*-$[CoCl(H_2O)(NH_3)_4]Cl_2$ is shown in Fig. 3, together with those of *cis*-$[CoCl(H_2O)(NH_3)_4]Br_2$ and *cis*-$[CoBr(H_2O)(NH_3)_4]Br_2$. The TG curve indicates that the deaquation-anation reaction proceeds in the temperature range of 135 to 170°C, and the DTA curve exhibits an endothermic peak corresponding to the deaquation-anation at 150°C. During the dehydration process, the color change from violet to bluish violet was first observed and then the bluish violet was gradually converted to green by heating for a long time, suggesting the formation of *trans*-complexes. From these results, the following stepwise reactions occur,

cis-$[CoCl(H_2O)(NH_3)_4]Cl_2 \rightarrow$ *cis*-$[CoCl_2(NH_3)_4]Cl$

$\rightarrow$ *trans*-$[CoCl_2(NH_3)_4]Cl$.

The thermal behavior of *cis*-$[CoBr(H_2O)(NH_3)_4]$-Cl_2 was analogous to that of *cis*-$[CoCl(H_2O(NH_3)_4]$-Cl_2, so far as the initiation temperature and the reaction product of the deaquation-anation reaction are concerned.

(e) cis-$[CoCl(H_2O)(NH_3)_4]Br_2$ *and* cis-$[CoBr(H_2O)(NH_3)_4]Br_2$*:* When these were heated, the following reactions were considered to occur,

cis-$[CoCl(H_2O)(NH_3)_4]Br_2 \rightarrow [CoClBr(NH_3)_4]Br$ (green)

cis-$[CoBr(H_2O)(NH_3)_4]Br_2 \rightarrow [CoBr_2(NH_3)_4]Br$ (green).

The color change from violet to green was found in both cases. The TG curves in Fig. 3 indicate that the mass loss of the bromoaquo-bromide and of the chloroaquo-bromide was completed at 130 and 135°C, respectively, whereupon the produced *trans*-complexes were decomposed. A single endothermic peak was observed at 120°C in both DTA curves, where the deaquation-anation reaction occurred.

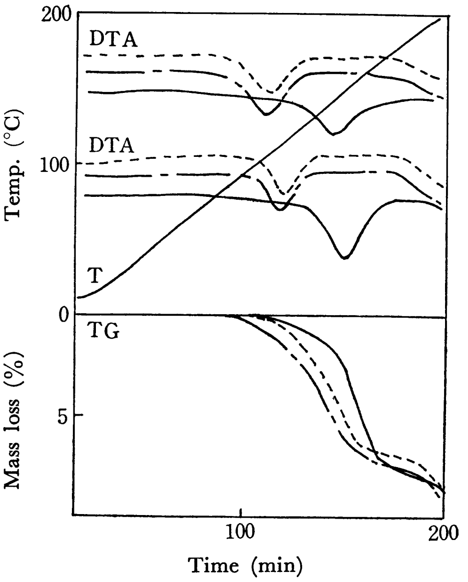

Fig. 3. Derivatograms of *cis*-$[CoCl(H_2O)(NH_3)_4]Cl_2$ (——), *cis*-$[CoCl(H_2O)(NH_3)_4]Br_2$ (———) and *cis*-$[CoBr(H_2O)$-$(NH_3)_4]Br_2$ (----).

Electronic Spectra. Deaquation-anation reactions of the complexes were followed and the reaction products were identified by measuring the electronic spectra. The electronic spectra of *cis*-$[CoBr(H_2O)en_2]$-$Br_2\cdot H_2O$ and of the related complexes are shown in Fig. 4.

When *cis*-$[CoBr(H_2O)en_2]Br_2\cdot H_2O$ is heated, the first absorption maximum is gradually shifted from 530 nm ($\varepsilon=102.0$) to considerably lower frequency side. After the deaquation-anation was completed, the reaction product gave the broad absorption band at 554 nm with less intense shoulder at 630—650 nm. This suggests the superposition of spectra of *cis*-$[CoBr_2$-

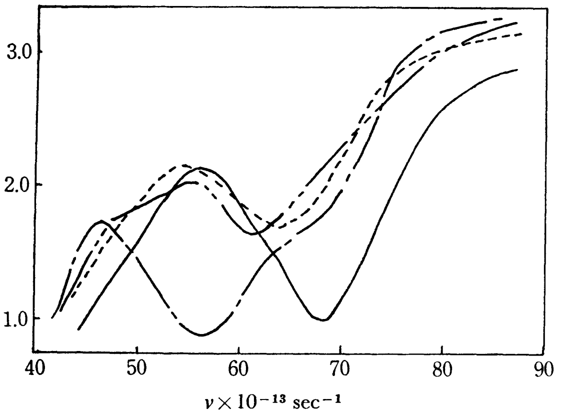

Fig. 4. Electronic spectra of *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$ (——), *cis*-$[CoBr_2en_2]Br \cdot H_2O$ (----), *trans*-$CoBr_2en_2]Br$ (– – –) and of thermal reaction product of *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$ (— — —).

$en_2]^+$ and *trans*-$[CoBr_2en_2]^+$, which showed the first absorption maxima at 554 nm ($\varepsilon = 101.0$) and at 655 nm ($\varepsilon = 55.1$), respectively, as shown in Fig. 4. In the present work, no attempt was made to isolate the two isomers from the mixture.

The absorption spectra of *cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$ and of the related complexes are shown in Fig. 5, which displays that the heating of *cis*-$[CoCl(H_2O)en_2]Br \cdot H_2O$ also gives the formation of the mixture of *trans*-$[CoClBren_2]Br$ and *cis*-$[CoClBren_2]Br$ as similar as that of *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$.

When the bromide-nitrate complex, *cis*-$[CoCl(H_2O)en_2]Br(NO_3)$, was heated, the first absorption peak of *cis*-complex disappeared and the same absorption spectrum as found for *trans*-$[CoClBren_2]NO_3$ was obtained.

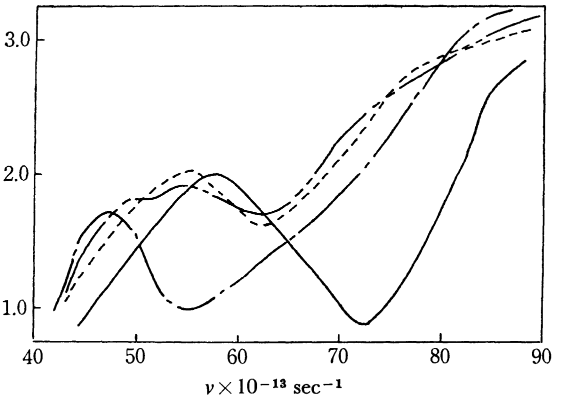

Fig. 5. Electronic spectra of *cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$ (——), *cis*-$[CoClBren_2]Br \cdot H_2O$ (----), *trans*-$[CoClBren_2]Br$ (– – –) and of thermal reaction product of *cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$ (— — —).

The deaquation-anation reactions for the ammine-complexes, (d) and (e), were only followed by the observation of their color change.

Rate Studies. Isothermal dehydration of *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$ was followed by using a thermobalance at several constant temperatures in the range of 92 to 120°C and the conversion ratios this complex to *cis*-$[CoBr_2en_2]Br$ and to the corresponding *trans*-complex were determined spectrophotometrically by the method described in the experimental section.

The dehydration reactions of all the monoacidoaquo-complexes treated in the present work were found to proceed in the first order. For example, the rate constant for the deaquation-anation reaction of *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$ is expressed by,

$$k_a = \frac{1}{t} \ln \frac{a}{a-x}$$

the rate constant concerning the formation of *cis*-$[CoBr_2en_2]Br$ by,

$$k_b = \frac{1}{t} \cdot \frac{y}{x} \ln \frac{a}{a-x}$$

and that concerning the formation of *trans*-$[CoBr_2en_2]Br$ by

$$k_c = \frac{1}{t} \cdot \frac{z}{x} \ln \frac{a}{a-x}$$

where a denotes the initial amount of the starting complex, *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$, x is the amount of the complex that has disappeared, y is the amount of *cis*-$[CoBr_2en_2]Br$ formed, and z is the amount of *trans*-$[CoBr_2en_2]Br$ formed in the time t. Since the plots, $\log a/(a-x) \sim t$, $(y/x) \log a/(a-x) \sim t$ and $(z/x) \log a/(a-x) \sim t$, give straight lines at each temperature as shown in Fig. 6, the above three reactions are considered to proceed in parallel with each other and in the first order respectively.

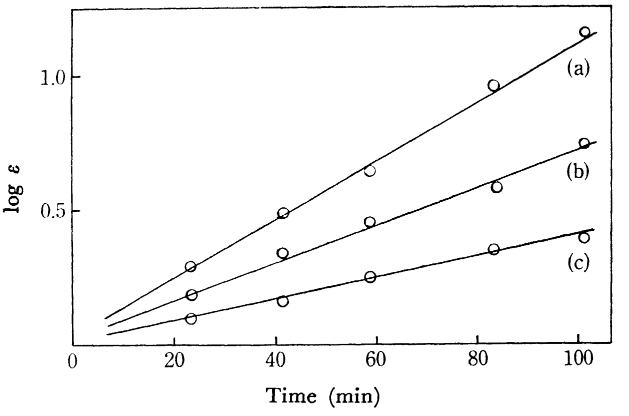

Fig. 6. The relationships of $\log a/(a-x)$ (a), $y/x \cdot \log a/(a-x)$ (b) and $z/x \log a/(a-x)$ (c) against t for deaquation-anation of *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$.

Rate constants calculated for *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O$ are listed in Table 2, together with those for only the dehydration of *cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$. The activation energies (E_a) were obtained from the temperature dependency of the rate constant, and entropies of activation (ΔS_a) were calculated by using "absolute rate theory", which are given in Table 3.

Taking into account for the data of the initiation temperatures of deaquation-anation reaction in Table 1 and those of the activation energies in Table 3, the order of the thermal stability is deduced to be, *cis*-$[CoCl(H_2O)en_2]Br(NO_3) >$ *cis*-$[CoBr(H_2O)en_2]Br_2 \cdot H_2O \approx$ *cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$ for halogenoaquo ethylenediamine complexes, and *cis*-$[CoCl(H_2O)(NH_3)_4]Cl_2 >$ *cis*-$[CoCl(H_2O)(NH_3)_4]Br_2 \approx$ *cis*-$[CoBr(H_2O)(NH_3)_4]$-

Table 2. Rate constants of deaquation-anation of *cis*-[$CoBr(H_2O)en_2$]$Br_2 \cdot H_2O$ and dehydration of *cis*-[$CoCl(H_2O)en_2$]$Br_2 \cdot H_2O$

Temp. (°C)	k_a (sec^{-1})	k_b (sec^{-1})	k_c (sec^{-1})	k_d [a] (sec^{-1})
92	$(1.9\pm0.3)\times10^{-4}$	$(1.2\pm0.3)\times10^{-4}$	$(7.2\pm0.3)\times10^{-5}$	$(2.4\pm0.3)\times10^{-4}$
100	$(2.3\pm0.3)\times10^{-4}$	$(1.4\pm0.3)\times10^{-4}$	$(8.5\pm0.3)\times10^{-5}$	$(2.8\pm0.3)\times10^{-4}$
110	$(1.3\pm0.2)\times10^{-3}$	$(7.5\pm0.3)\times10^{-4}$	$(4.8\pm0.3)\times10^{-4}$	$(1.7\pm0.2)\times10^{-3}$
120	$(3.5\pm0.4)\times10^{-3}$	$(2.2\pm0.4)\times10^{-3}$	$(1.2\pm0.4)\times10^{-3}$	$(4.0\pm0.3)\times10^{-3}$

a) k_d: rate constant for dehydration of *cis*-[$CoCl(H_2O)en_2$]$Br_2 \cdot H_2O$

Table 3. The thermochemical functions for deaquation-anation reactions

Complex	E_a (kcal/mol)	ΔH (kcal/mol)	ΔS^{a}_{a} (e. u.)	ΔS^{b}_{a} (e. u.)	ΔS^{c}_{a} (e. u.)
cis-[$CoCl(H_2O)en_2$]$Br_2 \cdot H_2O$	38±5	13.5±2.0			
cis-[$CoCl(H_2O)en_2$]$Br(NO_3)$	68±6	7.5±2.0			
cis-[$CoBr(H_2O)en_2$]$Br_2 \cdot H_2O$	37±5	13.3±2.0	16±5	15±5	15±5

ΔS^{a}_{a}: the disappearance for *cis*-[$CoBr(H_2O)en_2$]$Br_2 \cdot H_2O$, ΔS^{b}_{a}: the formation of *cis*-[$CoBr_2en_2$]Br, ΔS^{c}_{a}: the formation of *trans*-[$CoBr_2en_2$]Br.

Br_2 for halogenoaquoammine complexes.

The ratios of *cis*-[$CoBr_2en_2$]Br to *trans*-[$CoBr_2en_2$]Br in the products at all temperatures investigated were found to be 62 : 38 at the end of deaquation-anation.

The reaction products produced by the deaquation-anation reactions are considerably affected by the entering groups: *i.e.*, *cis*-[$CoCl(H_2O)en_2$]$Br_2 \cdot H_2O$, *cis*-[$CoBr(H_2O)en_2$]$Br_2 \cdot H_2O$ and *cis*-[$Co(H_2O)_2en_2$]$Br_3 \cdot 2H_2O$ gave the mixture of *cis*- and *trans*-complexes, while *cis*-[$CoCl(H_2O)en_2$]Cl_2 and *cis*-[$Co(H_2O)_2en_2$]$Cl_3 \cdot 2H_2O$ gave *cis*-[$CoCl_2en_2$]Cl with retention of structure.

As for the ammine-complexes, the reactions proceeded in the same manner as found for ethylenediamine-complexes: *i. e.*, *cis*-[$CoCl(H_2O)(NH_3)_4$]Cl_2 and *cis*-[$CoBr(H_2O)(NH_3)_4$]Cl_2 were deaquated with retention of structure to give the corresponding *cis*-complexes as reaction products, whereas *cis*-[$CoCl(H_2O)(NH_3)_4$]Br_2 and *cis*-[$CoBr(H_2O)(NH_3)_4$]Br_2 underwent *cis*-to-*trans* stereochemical change to give the corresponding *trans*-complexes as reaction products.

From these facts, it is concluded that, when the entering group is chloride ion, deaquation-anation reaction proceeds with the retention of structure, while, when it is bromide ion, the stereochemical change occurs during the deaquation-anation process. In addition, *cis*-[$CoCl(H_2O)en_2$]$Br(NO_3)$ was found to undergo the complete conversion into *trans* form. As seen in these complexes, the kind of counter ions in the outer coordination sphere affects the geometrical structure of deaquation-anation reaction products, though the kind of acidic ligands coordinated does not so much affect it.