April, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 1027—1031 (1976) 1027

Derivatographic Studies on Transition Metal Complexes. XVII.[1] Solid-phase Deaquation-anation of Some Optically Active Aqua–cobalt(III) Complexes[2]

Ryokichi Tsuchiya, Masakatsu Omote, Akira Uehara, and Eishin Kyuno
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

(Received December 17, 1975)

Stereochemical changes involved in the solid-phase deaquation-anation of the following optically active aqua-cobalt(III) complexes were investigated: $(+)_{546}$-*cis*-$[Co(H_2O)_2en_2]X_3\cdot 2H_2O$ (X=Cl or Br), $(+)_{589}$-*cis*-$[CoCl(H_2O)en_2]Cl_2\cdot H_2O$, $(-)_{589}$-*cis*-$[CoCl(H_2O)en_2]Br_2\cdot H_2O$, $(+)_{589}$-α-$[CoCl(H_2O)trien]Cl_2\cdot H_2O$ and $(+)_{589}$-α-$[CoCl(H_2O)trien]Br_2\cdot 2H_2O$, where en and trien denote ethylenediamine and triethylenetetramine, respectively. Thermal deaquation-anation processes for each complex were observed with a derivatograph, polarimeter, and UV and CD spectrophotometers. *cis*-$[Co(H_2O)_2en_2]Cl_3\cdot 2H_2O$ was converted into *cis*-$[CoCl(H_2O)en_2]Cl_2$ at first and then *cis*-$[CoCl_2en_2]Cl$; the stereochemical changes during the first step and the second step were found to be retention and racemization, respectively. In contrast, a predominant stereochemical change involved in the deaquation-anation of *cis*-$[Co(H_2O)_2en_2]Br_3\cdot 2H_2O$ was *cis*-to-*trans* isomerization. The deaquation-anation of *cis*-$[CoCl(H_2O)en_2]Cl_2\cdot H_2O$ and *cis*-$[CoCl(H_2O)en_2]Br_2\cdot H_2O$ was found to be accompanied by racemization and by greater parts of *cis*-to-*trans* isomerization, respectively. However, both α-$[CoCl(H_2O)trien]Cl_2\cdot H_2O$ and α-$[CoCl(H_2O)trien]Br_2\cdot 2H_2O$ undergo deaquation-anation with retention.

Werner found that *cis*- and *trans*-$[Co(H_2O)_2en_2]Cl_3$ evolve waters *in vacuo* or heating at 115 °C to yield the violet product *cis*-$[CoCl_2en_2]Cl$.[3] Chang and Wendlandt studied various *cis*- and *trans*-$[Co(H_2O)_2en_2]X_3$ complexes (X=Cl, Br or NO_3) from the standpoint of thermal deaquation-anation in the solid-phase. They suggested that the variation of the counter anions sometimes causes geometrical isomerization (*cis*↔*trans*) during the course of deaquation-anation.[4]

In addition to the isomerization, other stereochemical changes such as racemization should also be included during the course of deaquation-anation. However, no information has been obtained on such stereochemical changes, except for the report by Mathieu that (+)-*cis*-$[CoCl(H_2O)en_2]Cl_2$ racemizes when heated at 100 °C in the solid-phase.[5]

More detailed information would be obtained if optically active aqua-cobalt(III) complexes were employed for studying deaquation-anation.

We have undertaken to (1) derivatographically investigate the solid-phase deaquation-anation of three types of optically active aqua-cobalt(III) complexes: *cis*-$[Co(H_2O)_2en_2]X_3$, *cis*-$[CoCl(H_2O)en_2]X_2$ and α-$[CoCl(H_2O)trien]X_2$ (X=Cl or Br), and (2) obtain further information on the stereochemical changes during the course of deaquation-anation.

Experimental

Preparation of Complexes. $(+)_{546}$-*cis*-$[Co(H_2O)_2en_2]Cl_3\cdot 2H_2O$ (I) and $(+)_{546}$-*cis*-$[Co(H_2O)_2en_2]Br_3\cdot 2H_2O$(II) were prepared from optically active $[CoCO_3en_2]Cl$.[6]

Complex I, Found: C, 13.58; H, 6.86; N, 14.89%. Calcd for $[Co(H_2O)_2en_2]Cl_3\cdot 2H_2O$: C, 13.42; H, 6.71; N, 15.66%. $[\alpha]_{546}=300°$.

Complex II, Found: C, 10.27; H, 4.90; N, 11.42%. Calcd for $[Co(H_2O)_2en_2]Br_3\cdot 2H_2O$: C, 9.78; H, 4.94; N, 11.42%. $[\alpha]_{546}=200°$.

$(+)_{589}$-*cis*-$[CoCl(H_2O)en_2]Cl_2\cdot H_2O$ (III) and $(-)_{589}$-*cis*-$[CoCl(H_2O)en_2]Br_2\cdot H_2O$ (IV) were obtained through the resolution of racemic *cis*-$[CoCl(H_2O)en_2]Cl_2$ with ammonium (+)-3-bromocamphor-8-sulfonate ((+)-BCS).[7]

Complex III, Found: C, 15.10; H, 6.62; N, 17.43%. Calcd for $[CoCl(H_2O)en_2]Cl_2\cdot H_2O$: C, 14.94; H, 6.28; N, 17.43%. $[\alpha]_{589}=280°$.

Complex IV, Found: C, 11.87; H, 5.15; N, 13.32%. Calcd for $[CoCl(H_2O)en_2]Br_2\cdot H_2O$: C, 11.70; H, 4.88; N, 13.65%. $[\alpha]_{589}=-240°$.

$(+)_{589}$-α-$[CoCl(H_2O)trien]Cl_2\cdot H_2O$ (V) and $(+)_{589}$-α-$[CoCl(H_2O)trien]Br_2\cdot 2H_2O$ (VI) were prepared from α-$[CoCl_2trien]Cl$ and (+)-BCS.[8]

Complex V, Found: C, 20.68; H, 6.68; N, 15.95%. Calcd for $[CoCl(H_2O)trien]Cl_2\cdot H_2O$: C, 20.73; N, 16.12%. $[\alpha]_{589}=610°$.

Complex VI, Found: C, 16.08; H, 5.42; N, 12.68%. Calcd for $[CoCl(H_2O)trien]Br_2\cdot 2H_2O$: C, 15.78; H, 5.34; H, 5.34; N, 12.34%. $[\alpha]_{589}=590°$.

The other complexes, *cis*- and *trans*-$[CoCl_2en_2]Cl$,[9] $(+)_{589}$-*cis*-$[CoCl_2en_2]Cl\cdot H_2O$,[9] *cis*-$[CoBrClen_2]Br\cdot H_2O$,[10] *trans*-$[CoBrClen_2]NO_3$,[10] *cis*-$[CoBr_2en_2]Br\cdot H_2O$[11] and *trans*-$[CoBr_2en_2]NO_3$[11] were prepared in a manner similar to that described in literature, and they were used as the reference complexes.

Derivatographic Measurement. Measurements were carried out with a MOM Derivatograph Typ-OD-102 under constant flow of nitrogen at the heating rate of 1 °C/min. Five tenths grams of the samples was used in each run.

Spectral Measurement. Visible and UV, and CD spectra of the samples were recorded on a Hitachi Recording Spectrophotometer 322, and a JASCO Model DRD/UV-5 Spectrophotometer, respectively.

Polarimetric Measurement. Specific rotatory powers of the samples were measured with a JASCO Model DIP-SL Polarimeter.

Determination of the Ratios of cis- *to* trans-$[CoBr_2en_2]^+$ *and of* cis *to* trans-$[CoBrClen_2]^+$. The ratios of two isomers in the products after heating were determined spectrophotometrically in a manner similar to that reported previously.[12]

Results and Discussion

Diaquabis(ethylenediamine)cobalt(III) Complexes. $(+)_{546}$-cis-$[Co(H_2O)_2en_2]Cl_3\cdot 2H_2O$ *(I)*.[13] Figure 1 shows the derivatogram of complex I, together with that of $(+)_{546}$-*cis*-$[Co(H_2O)_2en_2]Br_3\cdot 2H_2O$ (II). We see that the complex evolves three moles of water at first at 46—75 °C and then one mole of water at

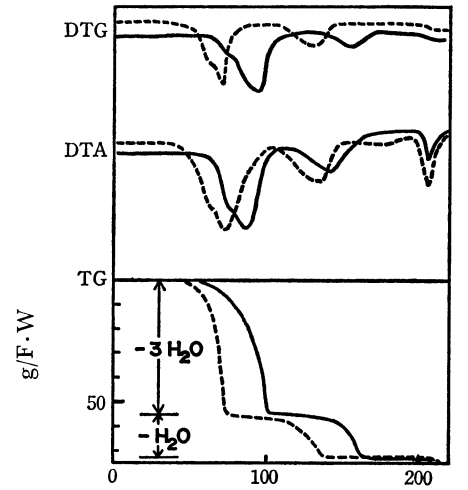

Fig. 1. Derivatograms of complexes I (----) and II (——).

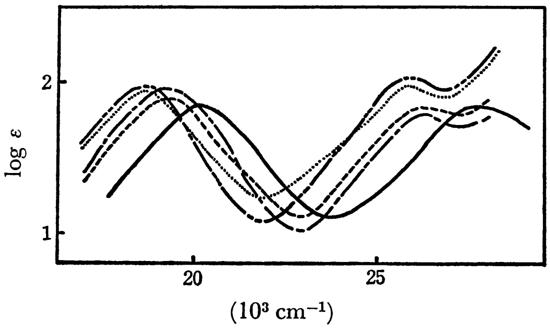

Fig. 2. Electronic spectra of complex I (——), the red-violet product (———), the violet product (······), and the reference complexes *cis*-$[CoCl(H_2O)en_2]Cl_2 \cdot H_2O$ (----) and *cis*-$[CoCl_2en_2]Cl \cdot H_2O$ (———).

112—138 °C. The initial red color of the complex turned red-violet at first and then violet in each dehydration step. The split DAT and DTG curves for the first water evolution step indicate that three moles of water are evolved in two steps.

Electronic spectra were measured in DMF solution to identify the red-violet and the violet products. Figure 2 shows the electronic spectra of complex I, the red-violet product, the violet product, and the reference complexes *cis*-$[CoCl(H_2O)en_2]Cl_2 \cdot H_2O$ and *cis*-$[CoCl_2en_2]Cl \cdot H_2O$. The numerical values for their absorption bands due to d-d transition are summarized in Table 1, together with those for the other series of complexes. Resemblance in the spectra between the red-violet product and *cis*-$[CoCl(H_2O)en_2]Cl_2 \cdot H_2O$ and between the violet product and *cis*-$[CoCl_2en_2]Cl \cdot H_2O$ proves that the original complex is converted successively into *cis*-$[CoCl(H_2O)en_2]Cl_2$ and then *cis*-$[CoCl_2en_2]Cl$.

CD spectra were measured to obtain information on the stereochemical changes of the complex during the course of deaquation-anation (Fig. 3). Figure 3(A) shows the CD spectra of complex I, the red-

Table 1. Absorption bands due to d-d transition (10^3 cm^{-1})

Complex	$\tilde{\nu}_{I}$		$\tilde{\nu}_{II}$
cis-$[Co(H_2O)_2en_2]X_3$ series[a]			
$(+)_{546}$-*cis*-$[Co(H_2O)_2en_2]Cl_2 \cdot 2H_2O$ (I)	20.20		28.10
Red-violet product	19.30		26.45
Violet product	18.66		25.57
cis-$[CoCl_2en_2]Cl \cdot H_2O$	18.64		25.52
$(+)_{546}$-*cis*-$[Co(H_2O)_2en_2]Br_3 \cdot 2H_2O$ (II)	20.20		28.10
First greenish violet product	15.27	18.18	*
Second greenish violet product	15.27	18.18	*
cis-$[CoBr_2en_2]Br \cdot H_2O$	18.10		*
trans-$[CoBr_2en_2]NO_3$	15.20	21.70(sh)[e]	*
cis-$[CoCl(H_2O)en_2]X_2$ series[a]			
$(+)_{589}$-*cis*-$[CoCl(H_2O)en_2]Cl_2 \cdot H_2O$ (III)	19.38		26.67
Violet product	18.66		25.57
$(-)_{589}$-*cis*-$[CoCl(H_2O)en_2]Br_2 \cdot H_2O$ (IV)	19.38		26.62
Greenish violet product	18.42	15.77	*
cis-$[CoBrClen_2]Br \cdot H_2O$	18.38		*
trans-$[CoBrClen_2]NO_3$	15.75		*
α-$[CoCl(H_2O)trien]X_2$ series[b]			
$(+)_{589}$-α-$[CoCl(H_2O)trien]Cl_2 \cdot H_2O$ (V)[c]	19.80		27.03
Violet product	18.48		26.30
α-$[CoCl_2\ trien]Cl$[d]	18.52		26.32
$(+)_{589}$-α-$[CoCl(H_2O)trien]Br_2 \cdot 2H_2O$ (VI)	19.84		27.10
Violet product	18.28		*

* These bands could not be clearly detected because of the overlap with the subsequent CT bands due to Br^- ions. a) Spectra measured in DMF. b) Spectra measured in water. c) Data identical with those reported in Ref. 16. d) Data cited from Ref. 16. e) sh denotes shoulder.

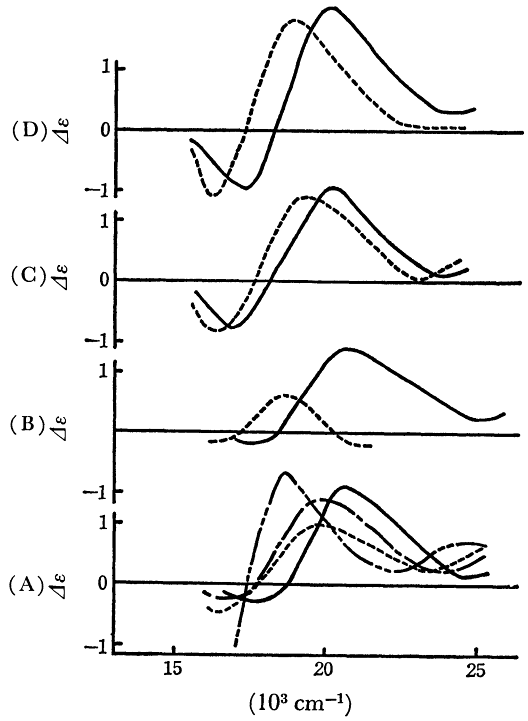

Fig. 3. CD spectra.
(A): complex I (——), the red-violet product (----), $(+)_{589}$-*cis*-$[\mathrm{CoCl(H_2O)en_2}]\mathrm{Cl_2\cdot H_2O}$ (—–—) and $(+)_{589}$-*cis*-$[\mathrm{CoCl_2en_2}]\mathrm{Cl\cdot H_2O}$ (—-—-—); (B): complex II (——) and the first greenish violet product (----); (C): complex V (——) and the violet product (----); (D): complex VI (——) and the violet product (----).

violet product and the reference complexes $(+)_{589}$-*cis*-$[\mathrm{CoCl(H_2O)en_2}]\mathrm{Cl_2\cdot H_2O}$ and $(+)_{589}$-*cis*-$[\mathrm{CoCl_2en_2}]$-$\mathrm{Cl\cdot H_2O}$. All the CD spectra show positive signs in similar patterns, indicating that the red-violet product still remains in an optically active form, the configuration during the process *cis*-$[\mathrm{Co(H_2O)_2en_2}]\mathrm{Cl_3\cdot 2H_2O}$→*cis*-$[\mathrm{CoCl(H_2O)en_2}]\mathrm{Cl}$ being retained. The measurements of CD spectra and specific rotatory powers demonstrate that the violet product is completely optically inactive.

The stereochemical changes during the deaquation-anation of complex I are summarized in Table 2; the first step *cis*-$[\mathrm{Co(H_2O)_2en_2}]\mathrm{Cl_3\cdot 2H_2O}$→*cis*-$[\mathrm{CoCl(H_2O)en_2}]\mathrm{Cl_2}$ involves retention and the second step *cis*-$[\mathrm{CoCl(H_2O)en_2}]\mathrm{Cl_2}$→*cis*-$[\mathrm{CoCl_2en_2}]\mathrm{Cl}$, racemization.

*$(+)_{546}$-*cis-*$[Co(H_2O)_2en_2]Br_3\cdot 2H_2O$ (II).* We see from the TG curve of the bromide (complex II, Fig. 1) that the mass losses of the complex take place in a pattern similar to that of the corresponding chloride (complex I) except that the former decomposes at somewhat higher temperatures than the latter. Complex II evolves three moles of water at 55—100 °C and then one mole of water at 130—162 °C. The complex changes to greenish violet from red, no further change being observed.

From the measurements of the electronic spectra of the greenish violet products obtained at the first and the second steps, it was found that both the products have two absorption bands at 15270 and 18180 cm^{-1}; these bands quite resemble the first bands of *trans*-$[\mathrm{CoBr_2en_2}]\mathrm{NO_3}$ (15200 cm^{-1}) and *cis*-$[\mathrm{CoBr_2en_2}]\mathrm{Br\cdot H_2O}$ (18100 cm^{-1}), respectively. Both the greenish violet products seem to consist of a mixture of *cis*- and *trans*-$[\mathrm{CoBr_2en_2}]^+$.

The ratios of *cis*- to *trans*-isomers in the product were determined spectrophotometrically in a manner similar to that reported previously.[12] It was found that both the products contain 23% *cis*- and 77% *trans*-isomers. In the case of the bromide, the *cis*-to-*trans* isomerization is a predominant stereochemical change involved in the deaquation-anation.

Such a *cis*-to-*trans* isomerization inevitably causes a considerable reduction in optical activity. However, CD spectral measurements should afford another information on the stereochemical changes. Figure 3(B) shows the CD spectra of complex II and the first and the second greenish violet products (the spectrum of the second product coincides with the base line). A small but clear positive sign is seen in the CD spectrum of the first product, but none was detected in that of the second product. This suggests that optical activities still remain in the first product, but not in the second product.

We see that the stereochemical change during the process *cis*-$[\mathrm{Co(H_2O)_2en_2}]\mathrm{Br_3\cdot 2H_2O}$→*cis*- and *trans*-$[\mathrm{CoBr_2en_2}]\mathrm{Br\cdot H_2O}$ involves most parts of *cis*-to-*trans* isomerization with small portions of retention and the remaining change in the process *cis*- and *trans*-$[\mathrm{CoBr_2en_2}]\mathrm{Br\cdot H_2O}$→*cis*- and *trans*-$[\mathrm{CoBr_2en_2}]\mathrm{Br}$ involves racemization (Table 2).

Chloroaquabis(ethylenediamine)cobalt(III) Complexes.

*$(+)_{589}$-*cis-*$[CoCl(H_2O)en_2]Cl_2\cdot H_2O$ (III).*[13] Figure 4 shows the derivatogram of complex III, together with that of $(-)_{589}$-*cis*-$[\mathrm{CoCl(H_2O)en_2}]\mathrm{Br_2\cdot H_2O}$ (IV). Complexes III and IV evolve two moles of water in analogous fashion to each other at 70—130 °C and 45—126 °C, respectively.

The original red-violet chloride (complex III) turned violet at the end of the liberation of two moles of water. Electronic spectral measurements showed that the $\tilde{\nu}_{\mathrm{I}}$ and $\tilde{\nu}_{\mathrm{II}}$ of the violet product appear at 18660 and 25570 cm^{-1}, these values being almost the

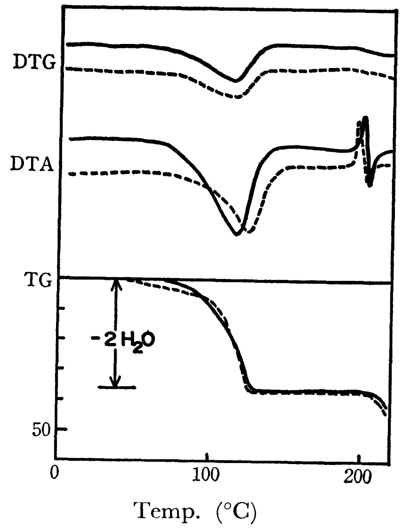

Fig. 4. Derivatograms of complexes III (——) and IV (----).

Table 2. Summary of the stereochemical changes involved in the deaquation-anation

Type of complex	X	Deaquation-anation process	Stereochemical change in the deaquation-anation
cis-$[Co(H_2O)_2en_2]X_3$ series	Cl	*cis*-$[Co(H_2O)_2en_2]Cl_3\cdot 2H_2O$ (I) red $\xrightarrow[46—75\ °C]{-3\ H_2O}$ (Step 1) *cis*-$[CoCl(H_2O)en_2]Cl_2$ red-violet	Step 1: retention
		$\xrightarrow[112—138\ °C]{-H_2O}$ (Step 2) *cis*-$[CoCl_2en_2]Cl$ violet	Step 2: racemization
	Br	*cis*-$[Co(H_2O)_2en_2]Br_3\cdot 2H_2O$ (II) red $\xrightarrow[55—100\ °C]{-3\ H_2O}$ (Step 1) *cis*- and ***trans***-$[CoBr_2en_2]Br\cdot H_2O$ greenish violet	Step 1: greater parts of *cis*-to-***trans*** isomerization with small parts of retention
		$\xrightarrow[130—162\ °C]{-H_2O}$ (Step 2) *cis*- and ***trans***-$[CoBr_2en_2]Br$ greenish violet	Step 2: racemization
cis-$[CoCl(H_2O)en_2]X_2$ series	Cl	*cis*-$[CoCl(H_2O)en_2]Cl_2\cdot H_2O$ (III) red-violet $\xrightarrow[70—130\ °C]{-2\ H_2O}$ *cis*-$[CoCl_2en_2]Cl$ violet	racemization
	Br	*cis*-$[CoCl(H_2O)en_2]Br_2\cdot H_2O$ (IV) red-violet $\xrightarrow[45—126\ °C]{-2\ H_2O}$ *cis*- and *trans*-$[CoBrClen_2]Br$ greenish violet	greater parts of *cis*-to-*trans* isomerization with small parts of racemization
α-$[CoCl(H_2O)trien]X_2$ series	Cl	α-$[CoCl(H_2O)trien]Cl_2\cdot H_2O$ (V) red-violet $\xrightarrow[38—105\ °C]{-2\ H_2O}$ α-$[CoCl_2trien]Cl$ violet	retention
	Br	α-$[CoCl(H_2O)trien]Br_2\cdot 2H_2O$ (VI) red-violet $\xrightarrow[50—85\ °C]{-2\ H_2O}$ (Step 1) α-$[CoCl(H_2O)trien]Br_2$ red-violet	Step 1: evolution of lattice water alone
		$\xrightarrow[85—124\ °C]{-H_2O}$ (Step 2) α-$[CoBrCl\ trien]Br$ violet	Step 2: retention

same as those (18640 and 25520 cm^{-1}) of *cis*-$[CoCl_2en_2]Cl\cdot H_2O$ (Table 1). From the CD spectra and specific rotatory powers, it was confirmed that the violet product is completely optically inactive.

It can be concluded in the case of complex III that the deaquation-anation proceeds with racemization, the result agreeing with that observed in the second step of the deaquation-anation of complex I.

*$(-)_{589}$-*cis*-$[CoCl(H_2O)en_2]Br_2\cdot H_2O$ (IV).* The bromide turned greenish violet from initial red-violet at the final stage of the evolution of two moles of water. As seen from Table 1, the electronic spectrum of the greenish violet product gives two peaks at 18.42 and 15.77 cm^{-1}, each of which satisfactorily agrees with the first bands of *cis*-$[CoBrClen_2]Br\cdot H_2O$ (18380 cm^{-1}) and *trans*-$[CoBrClen_2]NO_3$ (15750 cm^{-1}). This indicates that the greenish violet product is in the mixed form of *cis*- and *trans*-isomers. From the spectrophotometrical determination of the ratios of *cis*- to *trans*-isomers, it was found that the product contains 35% *cis*- and 65% *trans*-isomers.

If the configuration of the remaining *cis*-isomer were retained, the product should be, more or less, optically active. However, the measurements of CD spectra and specific rotatory powers revealed that the product is completely optically inactive. It seems that the stereochemical change during the deaquation-anation involves major parts of *cis*-to-*trans* isomerization with small portions of racemization.

Chloroaquatriethylenetetraminecobalt(III) Complexes.[13] Figure 5 shows the derivatograms of complexes V and VI. The chloride (complex V) loses two moles of water at 38—105 °C, turning violet from red-violet. The $\tilde{\nu}_I$ and $\tilde{\nu}_{II}$ for the violet product are respectively 18480 and 26300 cm^{-1}, which coincide with the values (18520 and 26320 cm^{-1}) for α-$[CoCl_2\ trien]Cl$. Figure

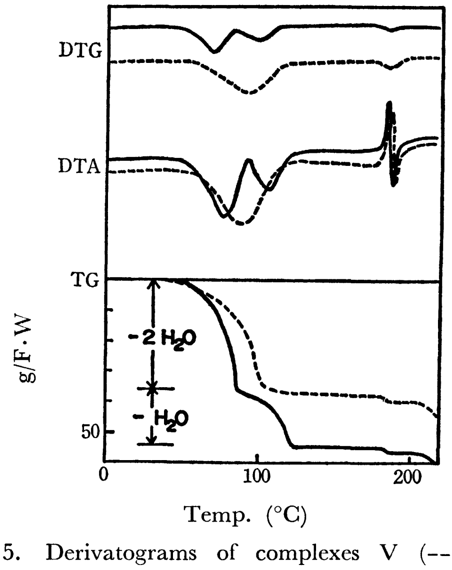

Fig. 5. Derivatograms of complexes V (----) and VI (——).

3(C) shows the CD spectra of the original chloride and the violet product. The CD spectrum of the violet product displays a positive sign similar to that of the original chloride. The measurement of the specific rotatory powers of the violet product indicates that the $[M]_D$ of the product is 2570° (Value of the reference complex α-$[CoCl_2$ trien]Cl: 2770°[8]). It can be concluded from these results that the stereochemical change during the deaquation-anation of complex V is retention.

On the other hand, the bromide (complex VI) evolves two moles of water at first at 50—85 °C and then one mole of water at 85—124 °C. The initial red-violet color of the complex remained unchanged at the first step, but changed to violet at the second step. The first step is probably simple evolution of lattice water and the second step may correspond to deaquation-anation. In the case of complex VI, the absence of the reference complexes such as α-[CoBrCltrien]$^+$ makes it impossible to identify the configuration of the violet product. However, the violet product may be regarded as optically active α-[CoBrCltrien]Br[14] for the following two reasons. Firstly, the spectrum pattern in the first band of the violet product was similar to that of α-$[CoCl_2$trien]Cl_2[8] (not shown) except that the $\tilde{\nu}_I$ of the violet product appears at slightly smaller wave number regions (18280 cm^{-1}) as compared with that (18520 cm^{-1}) of α-$[CoCl_2$trien]Cl. The slight shift may be due to the coordination of a Br^- ion as a consequence of the deaquation-anation. Secondly, the CD spectral changes observed during the deaquation-anation of complex VI are in the same tendency as that found in complex V (Fig. 3(C) and (D)). It might be concluded that the configuration is retained during the course of deaquation-anation.

LeMay and Bailar studied the solid-phase racemization of optically active *cis*-[Cr or $CoCl_2en_2]Cl\cdot H_2O$.[15] They tentatively interpreted the racemization in terms of an aquation-anation mechanism, but obtained no conclusive experimental evidence. Their suggestion may, however, be supported by our present result in which the racemization takes place in the process *cis*-$[CoCl(H_2O)en_2]Cl_2 \rightarrow$ *cis*-$[CoCl_2en_2]Cl$.

In the case of the bromides II and IV of the en complexes, the predominant stereochemical changes during the deaquation-anation are *cis*-to-*trans* isomerization, but the case is not the same for the corresponding trien complex.

As for the trien complexes V and VI, the configuration is retained irrespective of the kind of counter anions throughout the deaquation-anation. The trien complexes differ from the corresponding en complexes (the en complexes contain two chelate rings) as regards the inclusion of three fused chelate rings. Owing to the presence of the three fused chelate rings, the configuration of the trien complexes may be more tightly fixed than that of the en complexes.

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