Preparation and Solid-phase Thermal *cis-α* ⟷ *cis-β* Isomerization of the Chromium(III) Triethylenetetramine Complexes[1)]

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Heating of a mixture of $CrCl_3 \cdot 6H_2O$ and triethylenetetramine (trien) produced violet products which gave *cis*-α-$[Cr_2(OH)_2trien_2]X_4 \cdot 2H_2O$ and *cis*-α-$[Cr(OH)(H_2O)trien]X_2 \cdot H_2O$ (X=Cl, Br or I) on treatment with aqueous NaX solutions. *cis*-α-$[CrCl_2trien]Cl \cdot 2H_2O$ were obtained in the presence of a trace amount of water. Absolutely dry conditions are necessary for the preparation of *cis*-β-$[CrCl_2trien]Cl$. The thermally induced reversible *cis*-α↔*cis*-β isomerization was detected in the complexes *cis*-α-$[Cr(OH)(H_2O)trien]Cl_2 \cdot H_2O$ and *cis*-β-$[CrCl_2trien]Cl$ by means of derivatography and high-temperature IR spectroscopy. The former *cis*-α-hydroxoaqua complex was found to be converted irreversibly into *cis*-β-form above 225 °C in the solid-phase. The *cis*-β-form obtained readily isomerized to *cis*-α-form in aqueous media. The dimeric *cis*-α-$[Cr_2(OH)_2trien_2]^{4+}$ was converted gradually into the monomeric *cis*-α-$[Cr(OH)(H_2O)trien]^{2+}$ in water.

Three geometrically possible isomers are expected for the chromium(III)–triethylenetetramine (trien) complexes: *cis*-α, *cis*-β, and *trans*-forms (Fig. 1). In the case of the cobalt(III)[2–8)] and rhodium(III)[9,10)] complexes, the three geometrical isomers as well as other conformational isomers, especially of the dihalogeno complexes $[Co\ or\ Rh\ Cl_2\ trien]^+$ have been reported. As regards the chromium(III) complexes, however, only *cis*-α-form is known[11,12)] except for the recent report by Fordyce *et al.*[13)] on *cis*-β-$[CrCl_2trien]Cl$. This is partly because the *cis*-β complexes are apt to undergo rapid aquation and isomerization in aqueous media. Special care is thus necessary for preparation of the *cis*-β complexes. Difficulties might be overcome if hydrous chromium(III) salts could be used in the preparation of the desired complexes.

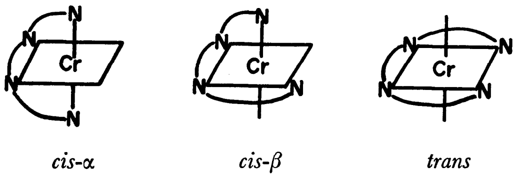

Fig. 1. Geometrically possible isomers of the Cr(III)–trien complexes.

We have attempted to prepare the Cr(III)–trien complexes by the reaction of $CrCl_3 \cdot 6H_2O$ and trien in a matrix state in order to clarify the solid-phase *cis*-α↔*cis*-β thermal isomerization of the complexes obtained. The survey of the isomerization in the solid-phase enables us to predict the possibility of the formation of *cis*-β complexes hardly obtainable in the presence of water.

Experimental

Preparation of Complexes. cis-α-*Di-μ-hydroxo-bis(triethylenetetraminechromium(III)) Iodide Dihydrate,* cis-α-$[Cr_2(OH)_2trien_2]I_4 \cdot 2H_2O$ *(bluish violet).* 30 g (0.11 mol) of chromium(III) chloride hexahydrate and 18 g (0.12 mol) of trien were triturated in a mortar of 12 cm diameter and heated at 180 °C for 6 h in an air-bath. The resulting violet masses were crushed. Excess ethanol was added to extract unreacted trien. After the extraction had been repeated 2 or 3 times, the bluish violet products were dissolved in 200 ml of hot water. Greenish residues were then removed by filtration. To the violet filtrate, 30 g (0.2 mol) of sodium iodide was added. Bluish violet crystals were soon separated out. The crystals had to be quickly recrystallized from water, otherwise the following hydroxoaqua complex was obtained. Yield about 20 g.

Found: C, 14.62; H, 4.15; N, 11.76%. Calcd for $C_{12}H_{42}O_4N_8I_4Cr_2$: C, 14.79; H, 4.08; N, 11.95%.

cis-α-*Hydroxoaquatriethylenetetraminechromium(III) Chloride Monohydrate,* cis-α-$[Cr(OH)(H_2O)trien]Cl_2 \cdot H_2O$ *(pink).* The violet filtrate was allowed to stand in a refrigerator overnight without addition of NaI, pink products being obtained. Recrystallization was carried out from water. Yield 3 g.

The complex was also obtained when the aqueous solution of the di-μ-hydroxo complex was allowed to stand overnight.

The corresponding bromide and iodide were obtained as monohydrates by addition of NaBr and NaI, respectively, to the aqueous solution of *cis*-α-$[Cr(OH)(H_2O)trien]Cl_2 \cdot H_2O$.

The *cis*-α complex was converted irreversibly into *cis*-β-form above 225 °C in the solid-phase. Isomerization makes it possible to prepare the *cis*-β complex. However, we could not purify the product because of the absence of a suitable solvent. Recrystallization from water always gave *cis*-α-form.

cis-α-*Dichlorotriethylenetetraminechromium(III) Chloride Dihydrate,* cis-α-$[CrCl_2trien]Cl \cdot 2H_2O$ *(violet) and* cis-β-*Dichlorotriethylenetetramine Chloride,* cis-β-$[CrCl_2trien]Cl$ *(violet).* These

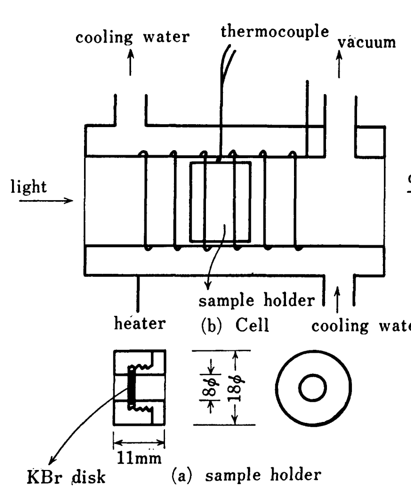

Fig. 2. Devices for measuring IR spectra at elevated temepartures.
(a) Sample holder, (b) cell.

were prepared from *cis*-α-[Cr(ox)trien]Br·nH$_2$O (n=3 or 0 respectively) according to the method of Fordyce *et al.*[13] slightly modified and identified by means of elemental analysis and IR spectroscopy. The striking difference in preparation between the *cis*-α and *cis*-β complexes is that the former can be obtained even in the presence of a trace amount of water, while water should be absolutely avoided in the preparation of the latter.

Instruments. Derivatograms, IR and UV spectra, and molar conductivities were measured by the same apparatus as reported.[14] The IR spectra at elevated temperatures were monitored with a temperature-controlled cell (Fig. 2). The cell was then set up on a JASCO A-3 IR spectrophotometer. The 9 mm diam KBr disk prepared in the usual way was loaded in the steel holder (Fig. 2-(a)), which was then put in a cell regulated at the desired constant temperatures (Fig. 2-(b)). The sample (KBr disk) temperature was measured and controlled with a SINYO RIKA DIGICON-1200 equipped with an alumel-chromel thermocouple.

Results and Discussion

IR Spectra. The band due to the NH asymmetric bending vibration in the region 1550—1600 cm^{-1} is diagnostically useful for distinguishing *cis*-α from *cis*-β complexes: *cis*-α has one band, *cis*-β 2 or 3 bands in this region.[2,12,13] Figure 3 shows the IR spectra of *cis*-α-[CrCl$_2$trien]Cl·2H$_2$O, *cis*-α-[Cr(ox)trien]Br·3H$_2$O, *cis*-α-[Cr(OH)(H$_2$O)trien]Cl$_2$·H$_2$O and *cis*-β-[CrCl$_2$trien]Cl. The spectrum of *cis*-α-[Cr$_2$(OH)$_2$trien$_2$]I$_4$·2H$_2$O is omitted since it is essentially the same as that of *cis*-α-[Cr(OH)(H$_2$O)trien]Cl$_2$·H$_2$O. The numerical data for the samples before, during and after heating at appropriate temperatures are summarized in Table 1. All the *cis*-α complexes have a sharp band, while the *cis*-β complex has three distinctive peaks. Noticeable changes could be detected in the IR spectra of *cis*-α-[Cr(OH)(H$_2$O)trien]Cl$_2$·H$_2$O and *cis*-β-[CrCl$_2$trien]Cl at elevated temperatures. The changes thermally reversible may come from the reversible *cis*-α↔*cis*-β isomerization of these complexes.

Electronic Spectra. *Hydroxo Complexes*: The absorption maxima due to d-d transition of each complex are summarized in Table 2. The dimeric structure for *cis*-α-[Cr$_2$(OH)$_2$trien$_2$]I$_4$·2H$_2$O is supported by the appearance of the band at about 36.6×10^3 cm^{-1} (log $\varepsilon \approx 4.1$) assignable to the bridging OH groups.[15] The absorption maxima of the complex in water shift gradually to higher wavenumber regions. After being left to stand they became similar to those of *cis*-α-[Cr(OH)(H$_2$O)trien]Cl$_2$·H$_2$O, suggesting that the dimeric di-μ-hydroxo complex is gradually converted into the monomeric complex in water.

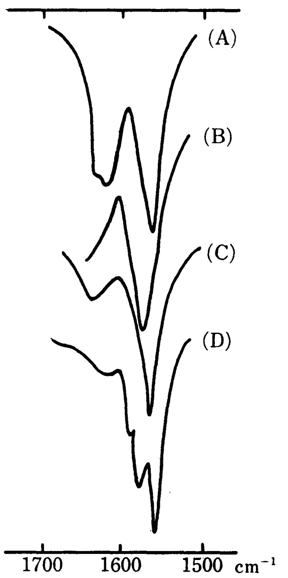

Fig. 3. IR spectra.
(A) *cis*-α-[CrCl$_2$trien]Cl·2H$_2$O, (B) *cis*-α-[Cr(ox)trien]Br·3H$_2$O, (C) *cis*-α-[Cr(OH)(H$_2$O)trien]Cl$_2$·H$_2$O, (D) *cis*-β-[CrCl$_2$trien]Cl.

Dichloro Complexes: The electronic spectra of *cis*-α-[CrCl$_2$trien]Cl·2H$_2$O and *cis*-β-[CrCl$_2$trien]Cl were measured both in dry methanol and in 0.1 mol dm^{-3} hydrochloric acid. The resemblance in color between the *cis*-α and *cis*-β complexes is recognizable from the similarity of their electronic spectral data in dry methanol used for preventing aquation of the complexes. However, both the complexes differ remarkably from each other in hydrochloric acid solution. As seen in Table 2, the first band (18.3×10^3 cm^{-1}) of the *cis*-β complex shifts to higher wavenumber regions (19.2×10^3 cm^{-1}) within only 3 minutes after the complex was dissolved in 0.1 mol dm^{-3} hydrochloric acid, the

Table 1. IR data for NH asymmetric bending vibration

Complex	Temp	Wave number (cm^{-1})[a]
cia-α-[CrCl$_2$trien]Cl·2H$_2$O	Room temp	1567 (vs)
cis-α-[Cr(ox)trien]Br·3H$_2$O	Room temp	1576 (vs)
cis-α-[Cr(OH)(H$_2$O)trien]Cl$_2$·H$_2$O	Room temp	1570 (vs)
	160 and 230 °C	1592 (w), 1575 (s), 1556 (vs)
	Cooled to room temp after heating at 160 °C	1570 (vs)
	Cooled to room temp after heating at 230 °C	1592 (w), 1575 (s), 1558 (vs)
cis-α-[Cr$_2$(OH)$_2$trien$_2$]I$_4$·2H$_2$O	Room temp	1568 (vs)
cis-β-[CrCl$_2$trien]Cl	Room temp	1591 (w), 1578 (s), 1561 (vs)
	70 °C—decomp temp (285 °C)	1581 (vs)
	Cooled to room temp after heating at 70—285 °C	1592 (w), 1579 (s), 1558 (vs)

a) The terms w, s, and vs denote weak, strong and very strong, respectively.

TABLE 2. ABSORPTION MAXIMA DUE TO d-d TRANSITION ($\tilde{\nu}\times10^3$ cm^{-1})

Complexes	$\tilde{\nu}_{\rm I}$(log ε)	$\tilde{\nu}_{\rm II}$(log ε)
cis-α-[$Cr_2(OH)_2trien_2$]$I_4\cdot2H_2O$		
in DMSO	18.4(2.11)	25.2(2.09)a)
in water	19.2(1.96)	25.9(1.85)
cis-α-[Cr(OH)(H_2O)trien]$Cl_2\cdot H_2O$		
in water	19.2(1.96)	25.9(1.85)
cis-α-[$CrCl_2$trien]Cl·$2H_2O$		
in dry methanol	18.5(2.00)	24.6(2.01)
in 0.1 mol dm^{-3} HClb)	18.6(2.01)	25.1(1.98)
cis-β-[$CrCl_2$trien]Cl		
in dry methanol	18.3(2.01)	24.6(1.95)
in 0.1 mol dm^{-3} HClb)	19.2(2.05)	25.3(1.89)c)

a) The complex gave the specific band at about 36.6×10^3 cm^{-1} (log $\varepsilon\approx4.1$) due to the di-μ-hydroxo group. b) Measured 3 min after the complex was dissolved. c) The data are closely similar to those of *cis*-α-[CrCl(H_2O)trien]$^{2+}$ reported previously.13)

spectrum being quite similar to those of *cis*-α-[CrCl(H_2O)trien]$^{2+}$.13) On the other hand, only a slight shift was observed in the case of the *cis*-α complex ($18.5\times10^3\rightarrow18.6\times10^3$ cm^{-1}). The *cis*-α complex was also found to be finally aquated to form *cis*-α-[CrCl(H_2O)trien]$^{2+}$. These results indicate that the *cis*-β complex aquates and isomerizes quite rapidly as compared with the *cis*-α complex.

Thermally Induced cis-α↔cis-β *Isomerization in the Solid-phase.* Reversible *cis*-α↔*cis*-β isomerization was found to be thermally induced in the complexes *cis*-α-[Cr(OH)(H_2O)trien]$Cl_2\cdot H_2O$ and *cis*-β-[$CrCl_2$trien]Cl. Figure 4 shows the derivatograms of both the complexes measured in a nitrogen stream at a heating rate of 1 °C min^{-1}.

As seen from the TG curve of *cis*-α-[Cr(OH)(H_2O)trien]$Cl_2\cdot H_2O$, the complex evolves 1 mol of water at 50—135 °C, remaining unchanged up to 295 °C, and then decomposes in a complicated way. Two small but distinct endothermic peaks are observed in the DTA curve after the dehydration step. The original pink color of the complex becomes slightly violet at the first endothermic peak (*ca.* 160 °C), the violet tone returning to the original pink color upon cooling at room temperature. The reversibility was repeatedly found in each step between the first (160 °C) and the second (225 °C) DTA peaks. However, thermochromism becomes irreversible above the temperature of the second DTA peak.

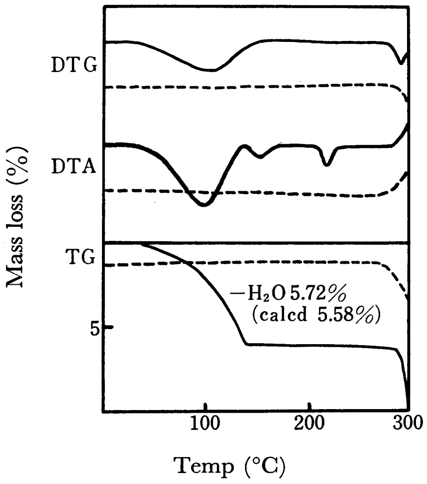

Fig. 4. Derivatograms of *cis*-α-[Cr(OH)(H_2O)trien]$Cl_2\cdot H_2O$ (——) and *cis*-β-[$CrCl_2$trien]Cl (----).

The thermochromic behavior was monitored by measuring IR spectra below and above respective DTA peaks. As seen from Table 1, the complex exhibits one sharp band at room temperature, and three bands (1592, 1575, and 1556 cm^{-1}) at 160 °C. The three bands were quenched when the complex was cooled to room temperature, its original one band being recovered. Such IR spectral changes were reversible between the first (160 °C) and the second (225 °C) DTA peaks. The changes became irreversible above 230 °C (Table 1). The results suggest that the complex undergoes reversible *cis*-α↔*cis*-β isomerization at 160—225 °C, being converted into *cis*-β-form irreversibly above 225 °C. This implies that the heating of the *cis*-α complex above 225 °C furnishes a useful method for preparing *cis*-β complex which is hardly obtained in solution. However, the *cis*-β complex thus obtained could not be purified.

cis-α-[Cr(OH)(H_2O)trien]$Cl_2\cdot H_2O$ underwent no olation upon heating, although hydroxoaqua Co(III) and Cr(III) complexes usually evolve the coordinated water to form the corresponding di-μ-hydroxo complexes.16)

On the other hand, the violet color of *cis*-β-[$CrCl_2$trien]Cl became faintly bluish above 70 °C, and the bluish tone returned to the initial violet when the complex was cooled to room temperature. The change was also reversible. No change was found in both the TG and DTA curves up to 285 °C, above which the complex began to decompose (Fig. 4).

Monitoring of the IR spectra revealed that the band due to the NH asymmetric bending vibration appears as three peaks (1591, 1578, and 1561 cm^{-1}) and as one sharp peak (1581 cm^{-1}) at room temperature and at a temperature above 70 °C, respectively. The one sharp peak, however, returned to three peaks when the complex was allowed to stand at room temperature. Such a spectral change was also reversible, suggesting the occurrence of the reversible *cis*-β↔*cis*-α isomerization. Fordyce *et al.*13) reported that the *cis*-β complex does not isomerize to *cis*-α-form even after the complex was held at 120 °C for 24 h. Their results are understandable in view of our finding that the isomerization is reversible in the temperature region from 70 °C to the decomposition temperature (285 °C). In contrast to *cis*-α-[Cr(OH)(H_2O)trien]$Cl_2\cdot H_2O$, no clear isomerization temperature was observed in the DTA curve of *cis*-β-[$CrCl_2$trien]Cl. This might be due to a small difference in their relative enthalpies between *cis*-β and *cis*-α complexes.

The isomerization of *cis*-α-[Cr(OH)(H_2O)trien]$Cl_2\cdot H_2O$ is completed at about 225 °C to give the *cis*-β complex, whereas the isomerization of *cis*-β-[$CrCl_2$trien]Cl remains to be reversible until the complex begins to decompose. This might be interpreted as follows: two adjacent coordination sites in octahedral environment are occupied by OH and H_2O in *cis*-α-[Cr(OH)(H_2O)trien]$Cl_2 \cdot H_2O$, and two chloride ions in *cis*-β-[$CrCl_2$-trien]Cl. The size of Cl ion is considerably greater than that of OH or H_2O. If isomerization takes place through twist-mechanism, the size of Cl ion hinders the completion of isomerization. Thus the *cis*-β dichloro complex might decompose prior to reaching the completion-temperature of isomerization. On the contrary, the completion-temperature (about 225 °C) of the isomerization of *cis*-α-[Cr(OH)(H_2O)trien]$Cl_2 \cdot H_2O$ is far lower than the decomposition temperature (295 °C).

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