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# Preparation and Solid-phase Thermal *cis-trans* Isomerization of the Mixed Bis(diamine)chromium(III) Complexes of the Type $[CrX_2(aa)(bb)]X\cdot nH_2O$[1]

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The mixed bis(diamine)chromium(III) complexes *trans*- and *cis*-$[CrX_2(aa)(bb)]X\cdot nH_2O$ were prepared and characterized where X is chloride or bromide ion; aa and bb are different diamines selected from ethylenediamine (en), propylenediamine (pn) and trimethylenediamine (tn); and *n* is a number of 0 to 2. The *cis-trans* isomerization of the above complexes was investigated non-isothermally (derivatographically) and isothermally in the solid-phase. The isomerization was found to be one-way (*trans*-to-*cis*) and exothermic. The activation energies were estimated for dehydration or dehydration plus dehydrohalogenation ($E_d$) and isomerization ($E_i$). The intermediates *mer*-$[CrBr_3(en)(pn)]\cdot 2H_2O$ and *mer*-$[CrBr_3(pn)(tn)]\cdot 2H_2O$ were isolated during the isomerization of *trans*-$[CrBr_2(en)(pn)]Br\cdot 2H_2O$ and *trans*-$[CrBr_2(pn)(tn)](H_5O_2)Br_2$, respectively. Bond rupture was proposed to be operative in the pathway of the isomerization.

We have already studied on the solid-phase *cis-trans* isomerizations of the bis(diamine)dihalogenochromium(III) complexes $[CrX_2(aa)_2]X$,[2–6] where X is chloride or bromide ion; aa is one of diamines such as ethylenediamine (en), propylenediamine (pn), 2,3-butanediamine (bn) and trimethylenediamine (tn). In the course of our studies, an interesting fact was noticed that the direction of isomerization (whether *trans*-to-*cis* or *cis*-to-*trans*) largely depends upon diamines contained in the complexes. Actually, *trans*-to-*cis* isomerization was recognized in the complexes containing en, pn or bn which is capable of forming five-membered chelate ring with chromium(III) ion, whereas *cis*-to-*trans* isomerization was found in the complexes containing tn which forms six-membered chelate ring. It is, therefore, of much interest to know the details of the isomerization of the complexes having a general formula $[CrX_2(aa)(bb)]X$ where X is the same as described above; aa and bb denote different diamines selected from en, pn, and tn. Among them, the complexes having the combination of five- and six-membered chelate rings are particularly interesting.

As for the chromium(III) complexes containing two different diamines, Pfeiffer *et al.* first reported the mixed tris(diamine) complexes $[Cr(en)_2(pn)]X_3$ ($X_3$=$Cl_3$, $(SCN)_3$, $I_3$, $[Cr(ox)_3]$, or $[Cr(CN)_6]$).[7] Recently, several mixed bis(diamine) complexes $[CrX_2(aa)(bb)]^+$ ($X_2$=$Cl_2$, $F_2$, $F(H_2O)$, and others) have been characterized and investigated from the viewpoint of hydrolysis kinetics.[8–12] In general, owing to large solubilities in common solvents, many troublesome steps are required to isolate the mixed bis(diamine) complexes as compared with the simple bis(diamine) complexes $[CrX_2(aa)_2]^+$.[13] The situation is rather severe for *cis* complexes than for *trans* complexes.

The present study was, therefore, undertaken (1) to prepare *trans*- and *cis*-mixed bis(diamine) complexes $[CrX_2(aa)(bb)]X$, and (2) to investigate the details of thermal *cis-trans* isomerization of the complexes in the solid-phase.

## Experimental

*Preparation of Complexes.* trans-$[CrCl_2(en)(pn)]Cl\cdot 0.75H_2O$ *(I)*, trans-$[CrCl_2(pn)(tn)]Cl\cdot H_2O$ *(II)*, trans-$[CrCl_2(en)(tn)](H_5O_2)Cl_2$ *(III)*, trans-$[CrBr_2(en)(pn)]Br\cdot 2H_2O$ *(IV)*, trans-$[CrBr_2(pn)(tn)](H_5O_2)Br_2$ *(V) and* trans-$[CrBr_2(en)(tn)](H_5O_2)Br_2$ *(VI)*: For the preparation of these complexes, the starting material *trans*-$[CrF_2(aa)(bb)]Br$ was first prepared by modifying the methods described earlier.[10,11] One gram of the material was dissolved in 10 ml of concentrated hydrochloric or hydrobromic acid and allowed to stand in a vacuum desiccator containing concentrated sulfuric acid as a desiccant, the desiccator being saturated with hydrogen chloride or hydrogen bromide by placing concentrated hydrochloric or hydrobromic acid in it. After a few days green crystals were separated. They were filtered, washed with ether and dried in a desiccator containing calcium chloride and *in vacuo* over KOH pellets for 2 h. The yields of the chloro complexes and the bromo complexes were about 60% and 65% based on the amounts of the starting materials used, respectively.

cis-$[CrCl_2(en)(pn)]Cl$ *(VII)*, cis-$[CrCl_2(en)(tn)]Cl$ *(VIII)*, cis-$[CrBr_2(en)(pn)]Br\cdot 2H_2O$ *(IX) and* cis-$[CrBr_2(pn)(tn)]Br\cdot H_2O$ *(X)*. The *cis* complexes were prepared by using thermal isomerization of the corresponding *trans* complexes in the solid-phase.

First of all, one gram of the corresponding *trans* complexes was triturated thoroughly in a mortar, spread thinly on watch glass and heated in an air-bath at given temperature for a given time. The optimum heating conditions (temperatures and heating times) for obtaining the *cis* complexes were determined non-isothermally (derivatographically) and isothermally. They were 60 min at 140 °C for complex VII, 30 min at 210 °C for complex VIII, 30 min at 125 °C for complex IX, and 70 min at 160 °C for complex X. The products thus obtained were allowed to cool to room temperature, dissolved in *N*,*N*-dimethylformamide (DMF) and filtered (if any insoluble materials remained). To the filtrate appropriate amounts of ether were added drop by drop with stirring, violet crystals being separated. They were filtered, washed with ether and air-dried. The yields of the *cis* complexes were about 40% based on the amounts of the starting *trans* complexes.

As mentioned in the later section, *trans*-$[CrCl_2(pn)(tn)]Cl\cdot H_2O$ (II) decomposed during isomerization at about 220 °C and *trans*-$[CrBr_2(en)(tn)](H_5O_2)Br_2$ (VI) decomposed at 170 °C without isomerization, and so attempts to get the corresponding *cis* complexes failed.

*Isolation of Intermediates during Isomerization.* $[CrBr_3(en)(pn)]\cdot 2H_2O$ *(XI) and* $[CrBr_3(pn)(tn)]\cdot 2H_2O$ *(XII).* They were isolated during isomerization of complexes IV and V. Each one gram of these complexes was spread in

TABLE 1. RESULTS OF ELEMENTAL ANALYSES

| Complexes | C% | | H% | | N% | |
|---|---|---|---|---|---|---|
| | Found | Calcd | Found | Calcd | Found | Calcd |
| I | 20.00 | 19.62 | 6.49 | 6.59 | 18.58 | 18.30 |
| II | 21.92 | 22.20 | 6.62 | 6.68 | 17.04 | 17.26 |
| III | 16.68 | 16.45 | 6.38 | 6.35 | 14.99 | 15.35 |
| IV | 12.23 | 12.98 | 4.27 | 4.70 | 11.46 | 12.11 |
| V | 12.58 | 12.99 | 4.36 | 4.49 | 9.81 | 10.07 |
| VI | 11.38 | 11.04 | 4.39 | 4.23 | 9.58 | 10.31 |
| VII | 20.54 | 20.53 | 6.19 | 6.20 | 19.13 | 19.15 |
| VIII | 20.25 | 20.53 | 6.37 | 6.20 | 19.14 | 19.15 |
| IX | 13.06 | 12.98 | 4.76 | 4.75 | 10.91 | 11.91 |
| X | 15.65 | 15.71 | 4.43 | 4.80 | 11.30 | 12.20 |
| XI | 12.20 | 12.98 | 4.41 | 4.76 | 11.53 | 12.11 |
| XII | 14.52 | 15.11 | 4.48 | 5.03 | 11.85 | 11.75 |

thin layer on watch glasses and heated for 25 min at 112 °C and 20 min at 150 °C, respectively. The products thus obtained were repeatedly washed with DMF until the washings became colorless. They were then washed with ether and air-dried. Bluish products were obtained with the yields of about 30%. The lattice waters in the crystals probably came from trace amounts of water present in the solvents employed in the procedures. Table 1 summarizes the results of elemental analyses.

*Non-isothermal Measurements.* Non-isothermal measurements were carried out with a Derivatograph Typ-OD-102 and the enthalpy changes, $\Delta H$, for dehydration and isomerization were evaluated as previously described.[14]

*Isothermal Measurements.* The rates of dehydration or dehydration plus dehydrohalogenation of complexes I through VI were determined at different temperatures with a CHYO 1001 thermobalance.

The rates of isomerization were followed by measuring the changes in absorbancies for the samples heated in an Abderhalden apparatus or an Ikemoto Rika Kogyo air-bath at various temperatures. Electronic spectra were monitored on a Hitachi Recording Spectrophotometer. The solvent used is DMF, dimethyl sulfoxide (DMSO), or 0.1 mol dm$^{-1}$ HCl, HBr, or HClO$_4$ solution. The isomerization ratios were calculated by using the following simultaneous equations:

$$\left.\begin{array}{l} 34.6x + 76.1y = D_{400} \\ 10.0x + 74.1y = D_{530} \end{array}\right\} \text{ for complexes I and VII}$$

$$\left.\begin{array}{l} 38.2x + 60.3y = D_{400} \\ 5.8x + 63.4y = D_{520} \end{array}\right\} \text{ for complexes III and VIII}$$

$$\left.\begin{array}{l} 53.8x + 12.0y = D_{540} \\ 39.8x + 29.3y = D_{390} \end{array}\right\} \text{ for complexes IV and IX}$$

$$\left.\begin{array}{l} 33.9x + 6.9y = D_{520} \\ 22.7x + 33.9y = D_{440} \end{array}\right\} \text{ for complexes V and X}$$

where $x$ and $y$ are the molar concentrations of *cis*- and *trans*-isomers, the numerical factors are the molar extinction coefficients of pure *cis*- and *trans*-isomers, and $D$'s represent the observed absorbancies at the wavelengths specified by the subscripts. Figure 1 shows, as an example, the electronic spectra of complexes I and VII.

*Thin Layer Chromatography (TLC).* TLC was employed to distinguish the mixed bis(diamine) complexes *trans*-[CrX$_2$(aa)(bb)]X from the simple bis(diamine) complexes *trans*-[CrX$_2$(aa)$_2$]X and *trans*-[CrX$_2$(bb)$_2$]X.[10,15] TLC plates used were those of silica gel 60F-254 made by Merck Ltd. Table 2 lists up the results of complexes I through VI together with those of the simple bis(diamine) complexes.

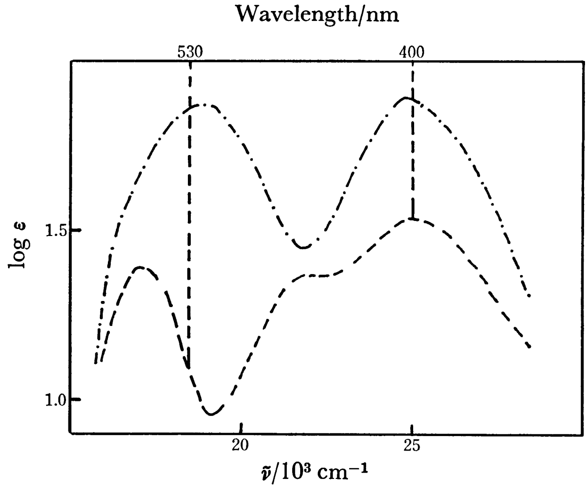


Fig. 1. Electronic spectra of complex I (----) and complex VII (—·—).

TABLE 2. RESULTS OF THIN LAYER CHROMATOGRAPHY FOR *trans*-[CrX$_2$(aa)$_2$]X, *trans*-[CrX$_2$(aa)(bb)]X, AND *trans*-[CrX$_2$(bb)$_2$]X[a)]

| | | | |
|---|---|---|---|
| | [CrCl$_2$en$_2$](H$_5$O$_2$)Cl$_2$ | [CrCl$_2$(en)(pn)]Cl·0.75H$_2$O | [CrCl$_2$pn$_2$]Cl·1.5H$_2$O |
| $R_f$ | 0.31 | 0.37 | 0.43 |
| | [CrCl$_2$pn$_2$]Cl·1.5H$_2$O | [CrCl$_2$(pn)(tn)]Cl·H$_2$O | [CrCl$_2$tn$_2$]Cl·0.5H$_2$O |
| $R_f$ | 0.57 | 0.54 | 0.50 |
| | [CrCl$_2$tn$_2$]Cl·0.5H$_2$O | [CrCl$_2$(en)(tn)](H$_5$O$_2$)Cl$_2$ | [CrCl$_2$en$_2$](H$_5$O$_2$)Cl$_2$ |
| $R_f$ | 0.55 | 0.48 | 0.43 |
| | [CrBr$_2$en$_2$]Br·H$_2$O | [CrBr$_2$(en)(pn)]Br·2H$_2$O | [CrBr$_2$pn$_2$]Br·H$_2$O |
| $R_f$ | 0.69 | 0.74 | 0.86 |
| | [CrBr$_2$pn$_2$]Br·H$_2$O | [CrBr$_2$(pn)(tn)](H$_5$O$_2$)Br$_2$ | [CrBr$_2$tn$_2$]Br·2H$_2$O |
| $R_f$ | 0.86 | 0.84 | 0.82 |
| | [CrBr$_2$tn$_2$]Br·2H$_2$O | [CrBr$_2$(en)(tn)](H$_5$O$_2$)Br$_2$ | [CrBr$_2$en$_2$]Br·H$_2$O |
| $R_f$ | 0.82 | 0.76 | 0.69 |

a) The mixture of acetic acid and methanol (9 : 1) was used as the eluent. For the chloro complexes, single plate is employed in each run (as given in each row), whereas for the bromo complexes two plates are used: one is for the simple bis(diamine) complexes and the other for the mixed bis(diamine) complexes.

Comparison of the $R_f$ values in the table reveals that the values for *trans*-$[CrX_2(aa)(bb)]X$ are just in between those for *trans*-$[CrX_2(aa)_2]X$ and *trans*-$[CrX_2(bb)_2]X$, indicating that all the mixed bis(diamine) complexes are pure.

## Results and Discussion

*Derivatography. Dehydration or Dehydration plus Dehydrohalogenation*: Figure 2 shows the derivatograms of the chloro complexes I, II, and III, and Fig. 3, those of the bromo complexes IV, V, and VI. Complexes I and II are dehydrated at 70—160 °C and 40—120 °C, respectively. Complex IV evolves 2 mol of water at two separate stages (40—103 °C and 125—158 °C). Complexes III, V, and VI lose 2 mol of water and 1 mol of hydrogen halide (dehydration plus dehydrohalogenation) at temperatures below 140 °C. The enthalpy changes, $\Delta H$, for dehydration or dehydration plus dehydrohalogenation for complexes I to VI were determined to be 17, 42, 55, 43, 49, and 57 kJ mol$^{-1}$, respectively.

*Isomerization.* Complexes I, II, III, and V give small but clear exothermic DTA peaks at 200, 220, 235, and 195 °C respectively, and they change in color from green to violet. This indicates that the isomerization takes place. Complex II partially decomposed during the isomerization, and therefore isolation of the corresponding *cis* complex was not possible. Prominent peak only due to mere isomerization can not be seen in the DTA curve of complex IV because the isomerization stage (90—130 °C) overlaps with the first dehydration stage (40—103 °C). Complex VI, after dehydration plus dehydrohalogenation (38—135 °C), remained unchanged up to about 170 °C, after that it melted and decomposed rapidly without isomerization.

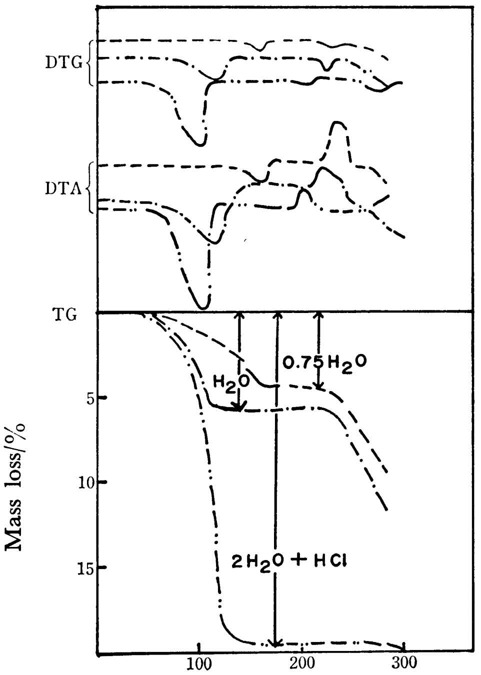


Fig. 2. Derivatograms of complex I (----), complex II (—·—) and complex III (—··—).

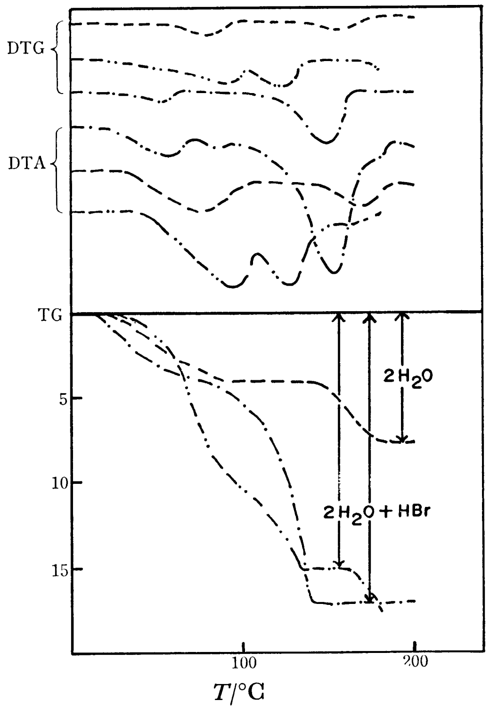


Fig. 3. Derivatograms of complex IV (----), complex V (—·—) and complex VI (—··—).

It must be noted that the *cis* complexes in the present study did not isomerize upon heating. We expected at the beginning of this study that the mixed bis(diamine) complexes having the composition of $[CrX_2(en)$ (or pn)(tn)]X might undergo both *trans*-to-*cis* and *cis*-to-*trans* isomerization. The expectation is based on the fact that *trans*-to-*cis* isomerization was recognized in the case of the simple bis(diamine) complexes $[CrX_2en_2$(or $pn_2$, $bn_2$)]X where en, pn, or bn forms five-membered chelate ring,[2-4] whereas only *cis*-to-*trans* isomerization was detected in the complexes $[CrX_2tn_2]X$ in which tn forms six-membered chelate ring.[5,6] However, as mentioned above, the isomerization in the present case was found to be one-way (*trans*-to-*cis*).

*Rate of Dehydration or Dehydration plus Dehydrohalogenation.* If the rate of dehydration or dehydration plus dehydrohalogenation at each temperature obeys the first order law, the following equation should hold:

$$2.303 \log a/(a-x) = k_d t$$

where $a$ is the initial amount of the starting complex, $x$ is the amount of dehydrated or dehydrated plus dehydrohalogenated product formed during time $t$, and $k_d$ is rate constant. Table 3 contains $k_d$ and the rate constants of isomerization ($k_i$). Linear relationships were obtained when $\log a/(a-x)$ were plotted against time $t$. From the Arrhenius plots, the activation energies for dehydration of complexes I and II were obtained as 67 and 76 kJ mol$^{-1}$. For complex IV, the activation energies for the first and second dehydration steps were 46 and 103 kJ mol$^{-1}$ respectively. The dehydration plus dehydrohalogenation stages of complexes III, V, and VI had the activation energies of 55, 112, and 30 kJ mol$^{-1}$ respectively.

*Rate of Isomerization.* The isomerization of complexes I, III, IV, and V was traced spectrophotom-

TABLE 3. RATE CONSTANTS OF DEHYDRATION OR DEHYDRATION PLUS DEHYDROHALOGENATION ($k_d$) AND ISOMERIZATION ($k_i$) AT VARIOUS TEMPERATURES

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Complex I | | | | | | | | | | | | | |
| $t$/°C | 100 | 109 | 120 | 130 | 138 | 153 | 159 | 172 | | | | | |
| $k_d \times 10^4$/s$^{-1}$ | 4.27 | 7.48 | 12.7 | 21.7 | | | | | | | | | |
| $k_i \times 10^4$/s$^{-1}$ | | | | | 0.24 | 1.22 | 2.22 | 7.70 | | | | | |
| Complex II | | | | | | | | | | | | | |
| $t$/°C | 73 | 86 | 94 | 103 | 113 | | | | | | | | |
| $k_d \times 10^4$/s$^{-1}$ | 1.92 | 4.99 | 9.21 | 13.3 | 26.9 | | | | | | | | |
| Complex III | | | | | | | | | | | | | |
| $t$/°C | 80 | 87 | 99 | 108 | 205 | 214 | 222 | 238 | | | | | |
| $k_d \times 10^4$/s$^{-1}$ | 6.73 | 9.60 | 17.6 | 25.6 | | | | | | | | | |
| $k_i \times 10^4$/s$^{-1}$ | | | | | 0.81 | 1.95 | 3.95 | 15.3 | | | | | |
| Complex IV | | | | | | | | | | | | | |
| $t$°/C | 70 | 78 | 89 | 100 | 130 | 138 | 146 | 153 | 100 | 108 | 111 | 116.5 | 125 |
| $k_d \times 10^4$/s$^{-1}$ | 2.56 | 4.67 | 5.76 | 9.12 | 8.47 | 13.9 | 26.6 | 44.1 | | | | | |
| $k_i \times 10^4$/s$^{-1}$ | | | | | | | | | 0.96 | 1.66 | 2.88 | 4.80 | 10.4 |
| Complex V | | | | | | | | | | | | | |
| $t$/°C | 110 | 115 | 120 | 126 | 133 | 138 | 151 | 156 | 161 | 168 | | | |
| $k_d \times 10^4$/s$^{-1}$ | 0.55 | 0.84 | 1.42 | 2.24 | 3.99 | | | | | | | | |
| $k_i \times 10^4$/s$^{-1}$ | | | | | | 0.56 | 1.41 | 2.52 | 4.08 | 7.20 | | | |
| Complex VI | | | | | | | | | | | | | |
| $t$°/C | 80 | 89 | 100 | 110 | 118 | | | | | | | | |
| $k_d \times 10^4$/s$^{-1}$ | 3.22 | 4.32 | 5.28 | 6.97 | 9.90 | | | | | | | | |

TABLE 4. TEMPERATURE ($t_d$ AND $t_i$) AND ACTIVATION ENERGIES ($E_d$ AND $E_i$)[a)]

| Complex | Dehydration or dehydration plus dehydrohalogenation | | Isomerization | |
|---|---|---|---|---|
| | $t_d$ | $E_d$ | $t_i$ | $E_i$ |
| | °C | kJ mol$^{-1}$ | °C | kJ mol$^{-1}$ |
| I | 102 | 67 | 167 | 155 |
| II | 86 | 76 | — | — |
| III | 76 | 55 | 224 | 181 |
| IV | 83 | 46103 | 117 | 114 |
| V | 136 | 112 | 163 | 123 |
| VI | 95 | 30 | — | — |

a) $t_d$ and $t_i$ stand for dehydration (or dehydration plus dehydrohalogenation) temperatures and isomerization temperatures where $k_d$ and $k_i$ show a constant value ($5 \times 10^4$ s$^{-1}$). The constant value was taken for the convenience of comparison. $E_d$ and $E_i$ designate activation energies for dehydration (or dehydration plus dehydrohalogenation) and isomerization.

etrically. In a manner similar to that of dehydration, the value of $\log b/(b-y)$ were plotted against time $t$, where $b$ is the initial amount of the *trans* complex, and $y$ is the amount of the corresponding *cis* complex formed by isomerization. Linear relationships were obtained, and only in the case of complex IV the value of $\log b/(b-y)$ converged about 0.1, indicating that 20% of isomerization takes place during dehydration plus dehydrobromination and the remaining in the anhydrous state. Rate constants of isomerization ($k_i$) are given in Table 3. The activation energies of isomerization were estimated to be 155, 181, 114, and 123 kJ mol$^{-1}$ for complexes I, III, IV, and V, respectively. Table 4 summarizes $t_d$ and $E_d$ (temperature and activation energy for dehydration or dehydration plus dehydrohalogenation), and $t_i$ and $E_i$ (temperature and activation energy for isomerization). Comparison of these values between the chloro complexes (I, II, and III) and the bromo complexes (IV, V, and VI) discloses that the bromo complexes are in general more easily dehydrated and dehydrohalogenated than the corresponding chloro complexes; the same tendency may also be true for isomerization.

*Mechanism of Isomerization.* Several studies have been reported on the mechanism of solid-phase racemization of metal complexes; *e.g.*, twist mechanism was preferably accepted in the solid-phase racemization of tris(oxalato)metallate,[16,17)] and LeMay and Bailar reported that the solid-phase racemization of *l*-*cis*-$[CrCl_2en_2]Cl \cdot H_2O$ proceeds *via* aquation-anation mechanism.[18)] The study on the isotopic exchange of anhydrous *cis*- and *trans*-$[CoCl_2en_2]Cl^*$ showed that the Cl ion in inner-sphere is exchanged by the Cl* ion in outer-sphere in the solid-phase,[19)] implying that a bond rupture process may be included in the exchange.

We have noticed that the solid-phase *cis*-*trans* isomerization of the simple bis(diamine)chromium(III) complexes do not necessarily require the participation of lattice water unlike the corresponding cobalt(III) complexes,[20,21)] and the reaction is, in most cases, accompanied by a small but clear exothermic DTA peak.[2–6)] We tentatively speculated that a bond rupture may be involved in the isomerization.[3)] In this study, we succeeded in isolating the intermediates XI and XII during the isomerizations of complexes

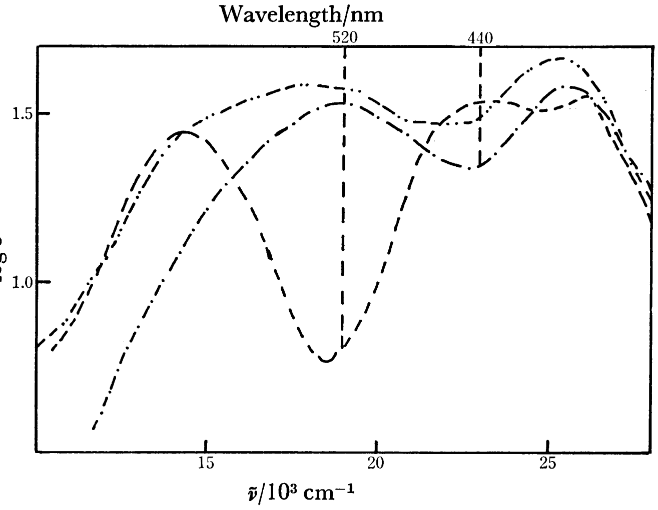
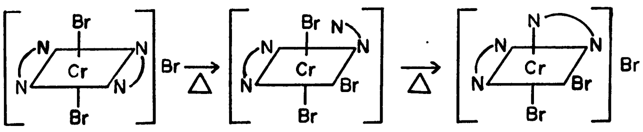


Fig. 4. Electronic spectra of complex V (----), complex X (—·—) and intermediate XII (—··—).



*trans* (green) intermediate (blue) *cis* (violet)

Fig. 5. Possible isomerization pathway.

IV and V as mentioned in the experimental section. Figure 4, as an example, shows the electronic spectra of complex V (*trans*-$[CrBr_2(pn)(tn)](H_5O_2)Br_2$), complex X (*cis*-$[CrBr_2(pn)(tn)]Br\cdot H_2O$) and the intermediate XII ($[CrBr_3(pn)(tn)]\cdot 2H_2O$). As seen from the figure, the *trans* complex V has, as expected, three absorption bands in the range of d-d transition [$14.2\times 10^3\ cm^{-1}$ ($\log \varepsilon=1.44$), $23.0\times 10^3\ cm^{-1}$ ($\log \varepsilon=1.53$) and $25.5\times 10^3\ cm^{-1}$ ($\log \varepsilon=1.51$)] and the *cis* complex X has two bands at $19.0\times 10^3\ cm^{-1}$ ($\log \varepsilon=1.53$) and $25.6\times 10^3\ cm^{-1}$ ($\log \varepsilon=1.58$). On the other hand, the intermediate XII has two bands at $18.0\times 10^3\ cm^{-1}$ ($\log \varepsilon=1.59$) and $24.6\times 10^3\ cm^{-1}$ ($\log \varepsilon=1.66$), but the first band is accompanied by two shoulders at $\approx 14.0\times 10^3\ cm^{-1}$ ($\log \varepsilon \approx 1.42$) and $\approx 21.0\times 10^3\ cm^{-1}$ ($\log \varepsilon \approx 1.48$). The occurrence of these shoulders in the first band, as has been reported in the studies on $[(Cr\ or\ Co)Cl_3dien]$[22] and $[CoCl_3(NH_3)_3]$,[23] supports that three bromide ions in the intermediate XII are arranged in *mer* position. The situation is also true for the intermediate XI (the spectral data were omitted because they were closely similar to those of the intermediate XII). From the above results, it is reasonable to consider that the isomerization of these complexes proceeds through a bond rupture pathway as represented in Fig. 5. It seems that the same mechanism is operative in the simple and mixed bis(diamine)chromium(III) complexes which isomerize with similar exothermic DTA peaks.

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