

field increases, the measured susceptibility decreases slightly and is probably due to a small net ferromagnetic moment which can arise in a canted system of antiferromagnetically coupled spins.

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Solid-Phase Thermal Cis-Trans Isomerization of Bis(diamine)chromium(III) Complexes Containing *d,l*-2,3-Butanediamine, *d,l*-1,2-Cyclohexanediamine, or *d,l*-2,4-Pentanediamine

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The bis(diamine)chromium(III) complexes *trans*- and *cis*-[CrX₂(aa)₂]X·*n*H₂O, where X is chloride or bromide ion, aa is a diamine selected from *d,l*-2,3-butanediamine (bn), *d,l*-1,2-cyclohexanediamine (chxn), or *d,l*-2,4-pentanediamine (ptn), and *n* = 1-3, were prepared, and their thermal cis-trans isomerizations were investigated both nonisothermally (derivatographically) and isothermally in the solid phase. The isomerization of the bn and chxn complexes was *trans*-to-*cis*, whereas that of the ptn complex was *cis*-to-*trans*. The enthalpy changes and activation energies were estimated for dehydration and/or dehydrohalogenation (ΔH_d and E_d) and for isomerization (ΔH_i and E_i). Bond rupture is proposed to be operative in the pathway of the isomerization from the facts that (1) the isomerization does not require the participation of lattice water, (2) the isomerization proceeds exothermically in all cases, and (3) the intermediate *mer*-[CrCl₃(bn)₂] was isolated during the isomerization of *trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O. The isomerization of the above complexes is also discussed in connection with that of the other related bis(diamine) complexes.

Introduction

Several studies have been carried out on the cis-trans isomerization of the simple bis(diamine)chromium(III) complexes [CrX₂(aa)₂]X² in the solid phase, where X is chloride or bromide ion and aa is ethylenediamine (en), *d,l*-1,2-propanediamine (pn), or 1,3-propanediamine (tn).³⁻⁶ *Trans*-to-*cis* isomerization was detected in the compounds containing en or pn, which are able to form a five-membered chelate ring with the chromium(III) ion, whereas *cis*-to-*trans* isomerization was recognized in the complexes containing tn, which forms a six-membered chelate ring. The mixed bis(diamine) complexes [CrX₂(aa)(bb)]X,² in which aa and bb are different diamines selected from en, pn, and tn, have recently been found to isomerize from *trans* to *cis* even with the complexes containing tn.⁷ More information is therefore needed to conclude that the diamines in the complexes play an important role in the direction of isomerization (whether it occurs *trans*-to-*cis* or *cis*-to-*trans*). The primary purpose of the present work is to investigate the details of the isomerization of the simple bis(diamine) complexes containing *d,l*-2,3-butanediamine (bn), *d,l*-1,2-cyclohexanediamine (chxn), or *d,l*-2,4-pentanediamine (ptn): the former two can form five-membered chelate rings, and the latter, a six-membered chelate ring.

In the cobalt(III) complexes in the same category, the isomerization was found to take place along with the dehydration of lattice water, and intermolecular aquation-anation was proposed to be a favorable mechanism for the reaction.⁸⁻¹¹ On the other hand, the previous studies pointed out that the chromium(III) complexes isomerize in the anhydrous state and the reaction always proceeds exothermically.³⁻⁶ These facts imply that some different mechanism (e.g., intramolecular bond rupture) may be operative in the reaction of the chromium(III) complexes. Another purpose of the present study is to clarify this implication in regard to the bn, chxn, and ptn chromium(III) complexes and to discuss the isomerization in connection with that of the other related complexes.

Experimental Section

Preparation of Diamines. The diamines bn¹² and ptn¹³ were prepared by the literature methods. chxn was available from Tokyo Kasei Kogyo Co., Ltd.

Preparation of Complexes. *trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O (I), *trans*-[CrBr₂(bn)₂]Br·HBr·2H₂O (II), *trans*-[CrCl₂(chxn)₂]Cl·HCl·2H₂O (III), and *trans*-[CrCl₂(ptn)₂]Cl·HCl·2H₂O (IV) were derived from *trans*-[CrF₂(aa)₂]ClO₄ (aa: bn, chxn, or ptn), which was prepared by modifying the methods described earlier.^{14,15} One gram of *trans*-[CrF₂(aa)₂]ClO₄ was dissolved in 10 mL of concentrated hydrochloric or hydrobromic acid and allowed to stand for about 12 h in the dark. The crude products thus obtained were collected by

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- (2) In this paper, the terms "simple bis(diamine) complexes" and "mixed bis(diamine) complexes" are used to express the dihalogenobis(diamine)chromium(III) complexes containing the same two diamines ([CrX₂(aa)₂]X) and those containing two different diamines ([CrX₂(aa)(bb)]X).
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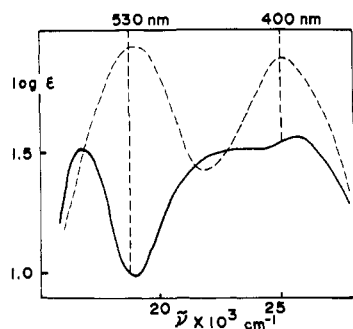


Figure 1. Electronic spectra of complexes II (—) and VII (---) in 0.1 mol dm⁻³ HNO₃.

filtration. They were dissolved in 10 mL of 2 mol dm⁻³ HCl or 20 mL of 0.5 mol dm⁻³ HBr and allowed to stand in a 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 obtained, which were filtered, washed with concentrated hydrochloric or hydrobromic acid, and dried in vacuo over KOH pellets for 2 h; yield about 0.3 g for the chloride and 0.4 g for the bromide.

trans-[CrCl₂(bn)₂]Br·H₂O (V) was prepared as follows: Two-tenths gram of crude *trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O (I) was dissolved in 10 mL of cold water, and thereto 0.4 g of sodium bromide was added. The products thus obtained were dissolved in 50 mL of methanol, to which 100 mL of ether was added drop by drop over 4 h to give green crystals. They were collected, washed with ether, and air-dried; yield 0.12 g.

cis-[CrCl₂(bn)₂]Cl·H₂O (VI), *cis*-[CrBr₂(bn)₂]Br·3H₂O (VII), *cis*-[CrCl₂(chxn)₂]Cl·2H₂O (VIII), and *cis*-[CrCl₂(ptn)₂]Cl·2H₂O (IX) were prepared according to published procedures.¹⁶

Isolation of Intermediate during Isomerization (*mer*-[CrCl₃(bn)₂]·H₂O (X)). One and eight-tenths gram of finely powdered *trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O (I) was spread in a thin layer on a watch glass and heated at 180 °C for 10 min. The products were thoroughly washed with water until the washings became colorless, washed with acetone and ether, and air-dried. The crude products were dissolved in 40 mL of dimethylformamide (DMF), and thereto 35 mL of ether was added gradually over about 3 h. Blue crystals were obtained, which were collected by filtration, washed with ether, and air-dried; yield 40 mg. The lattice water in the crystals probably came from trace amounts of water in the ether or DMF employed in the procedure.

Table I summarizes the analytical data for the complexes obtained.¹⁷

Nonisothermal Measurements. Nonisothermal measurements were carried out with a Typ-OD-102 MOM derivatograph, and the enthalpy changes for dehydration and/or dehydrohalogenation (ΔH_d) and for isomerization (ΔH_i) were estimated as previously described.¹⁸

Isothermal Measurements. The rate constants for dehydration and/or dehydrohalogenation (k_d) of the complexes were determined from weight changes at various temperatures by using a Chyo 1001 thermobalance.

The rate constants for isomerization (k_i) were followed by measuring the changes in absorbances for the samples heated in an Aberhalden apparatus or an Ikemoto Rika Kogyo air bath at various temperatures. Electronic spectra were monitored on a Hitachi recording spectrophotometer in 0.1 mol dm⁻³ HCl, HBr, HNO₃, and HClO₄ solutions and in DMF. The isomerization ratios were calculated by using the simultaneous equations

$$\left. \begin{aligned} 33.0x + 76.5y &= D_{400} \\ 9.6x + 84.8y &= D_{530} \end{aligned} \right\} \text{for complexes II and VII}$$

$$\left. \begin{aligned} 45.7x + 77.0y &= D_{400} \\ 16.9x + 83.0y &= D_{520} \end{aligned} \right\} \text{for complexes III and VIII}$$

$$\left. \begin{aligned} 48.2x + 44.8y &= D_{400} \\ 51.0x + 9.6y &= D_{525} \end{aligned} \right\} \text{for complexes IV and IX}$$

where x and y are the molar concentrations of *cis* and *trans* isomers,

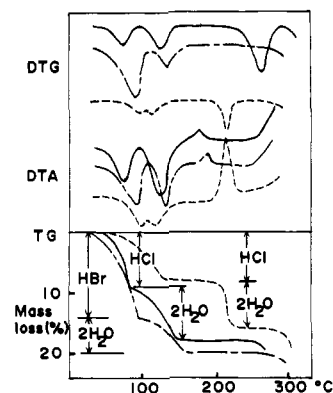


Figure 2. Derivatograms of complexes I (—), II (---), and III (· · ·).

the numerical factors are the molar extinction coefficients of the pure *cis* and *trans* isomers, and the D 's represent their absorbances at the wavelengths specified by each subscript. Figure 1 shows, as an example, the electronic spectra of complexes II and VII. The isomerization ratios are thus given by x (or y)/($x + y$). The activation energies for dehydration and/or dehydrohalogenation (E_d) and for isomerization (E_i) were calculated from the Arrhenius plots of the respective rate constants.

Results

First, it should be noted for clarification of the following discussion that *trans*-to-*cis* isomerization was detected for *trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O (I), *trans*-[CrBr₂(bn)₂]Br·HBr·2H₂O (II), *trans*-[CrCl₂(chxn)₂]Cl·HCl·2H₂O (III), and *trans*-[CrCl₂(bn)₂]Br·H₂O (V), and *cis*-to-*trans* isomerization was found only for *cis*-[CrCl₂(ptn)₂]Cl·2H₂O (IX).

Derivatography. Figure 2 shows the derivatograms of complexes I, II, and III. Complexes I and II evolve 1 mol of hydrogen chloride or hydrogen bromide at 55–80 °C and at 30–90 °C, respectively, and then 2 mol of water at 100–140 °C (complex I) and at 100–155 °C (complex II). The fact that the first evolution step corresponds to that of hydrogen chloride or hydrogen bromide was qualitatively confirmed by the occurrence of reaction with a silver nitrate solution. The color (green) of these complexes was unchanged in these steps. Although no change was found in the TG curves up to 240 °C (complex I) and 255 °C (complex II) after dehydration and/or dehydrohalogenation, small but clear exothermic DTA peaks appeared at 180 (complex I) and 190 °C (complex II), at which stages both the complexes changed in color to bluish violet and then to violet at 180–240 (complex I) and 190–255 °C (complex II). After that, they were decomposed above 240 and 255 °C in a complex reaction. We tried to isolate the intermediates during isomerization and as mentioned in the Experimental Section succeeded in obtaining the bluish violet [CrCl₃(bn)₂]·H₂O, in which one of two bn's is coordinated as unidentate toward chromium(III) ion.

On the other hand, the thermal reaction of complex III is slightly different from those of complexes I and II. The complex endothermically evolves 1 mol of hydrogen chloride at 40–140 °C and then exothermically 2 mol of water at 200–220 °C. The complex turned violet from the original green at the latter step. This seemingly implies that the isomerization takes place along with the dehydration. However, it was found from isothermal experiments that the isomerization and the dehydration occur at fairly close temperatures, but the isomerization precedes the dehydration just a little, the details of which are mentioned later.

Figure 3 shows the derivatograms of *trans*-[CrCl₂(bn)₂]Br·H₂O (V) and *cis*-[CrCl₂(ptn)₂]Cl·2H₂O (IX). As for complex V, 1 mol of water was lost at 50–110 °C and a plateau in the TG curve remained until the complex was decomposed above 260 °C. A small but clear exothermic peak is also seen in the DTA curve at about 200 °C, where the complex turned

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Table II. Rate Constants for Dehydration and/or Dehydrohalogenation (k_d) and Isomerization (k_i) at Various Temperatures^a

	<i>trans</i> -[CrCl ₂ (bn) ₂]Cl·HCl·2H ₂ O (I)												
<i>t</i> /°C	97	110	119	131	136								
10 ⁴ <i>k</i> _d (HCl + H ₂ O)/s ⁻¹	1.55	4.30	9.21	19.0	25.3								
	<i>trans</i> -[CrBr ₂ (bn) ₂]Br·HBr·2H ₂ O (II)												
<i>t</i> /°C	112	120	133	141	151	195	203	210	224	236			
10 ⁴ <i>k</i> _d (HBr + H ₂ O)/s ⁻¹	4.96	9.33	25.1	46.8	95.5								
10 ⁴ <i>k</i> _i /s ⁻¹						0.40	0.86	1.32	6.02	15.3			
	<i>trans</i> -[CrCl ₂ (chxn) ₂]Cl·HCl·2H ₂ O (III)												
<i>t</i> /°C	111	121	128	135	143	210	222	231	240	200	209	223	229
10 ⁴ <i>k</i> _d (HCl)/s ⁻¹	4.30	8.71	15.4	23.7	39.8								
10 ⁴ <i>k</i> _d (H ₂ O)/s ⁻¹						14.7	28.2	47.3	81.1				
10 ⁴ <i>k</i> _i /s ⁻¹										5.90	13.8	44.7	65.4
	<i>cis</i> -[CrCl ₂ (ptn) ₂]Cl·2H ₂ O (IX)												
<i>t</i> /°C	91	100	108	123	172	179	192	201					
10 ⁴ <i>k</i> _d (H ₂ O)/s ⁻¹	10.6	15.6	22.2	40.5									
10 ⁴ <i>k</i> _i /s ⁻¹					0.74	1.37	4.22	9.26					

^a (HCl + H₂O), (HBr + H₂O), (HCl), and (H₂O) stand for dehydrochlorination and dehydration, dehydrobromination and dehydration, dehydrochlorination, and dehydration, respectively.

Table III. Enthalpy Changes (ΔH_i) and Activation Energies (E_i) for Isomerization of the Simple and Mixed Bis(diamine) Complexes

complex	combination of members in chelate rings	direction of isomerization	ΔH_i /kJ mol ⁻¹	E_i /kJ mol ⁻¹	ref
Simple Bis(diamine) Complexes					
<i>trans</i> -[CrCl ₂ (en) ₂]Cl·HCl·2H ₂ O	5,5	trans to cis	<0 ^a	202	5
<i>trans</i> -[CrBr ₂ (en) ₂]Br·H ₂ O	5,5		<0 ^a	420	6
<i>trans</i> -[CrCl ₂ (pn) ₂]Cl·1.5H ₂ O	5,5		<0 ^a	193	5
<i>trans</i> -[CrBr ₂ (pn) ₂]Br·H ₂ O	5,5		<0 ^a	180	4
<i>trans</i> -[CrCl ₂ (bn) ₂]Cl·HCl·2H ₂ O (I)	5,5		-42	<i>b</i>	
<i>trans</i> -[CrBr ₂ (bn) ₂]Br·HBr·2H ₂ O (II)	5,5		-24	176	
<i>trans</i> -[CrCl ₂ (chxn) ₂]Cl·HCl·2H ₂ O (III)	5,5		<0 ^a	163	
Mixed Bis(diamine) Complexes					
<i>trans</i> -[CrCl ₂ (en)(pn)]Cl·0.75H ₂ O	5,5	trans to cis	<0 ^a	155	7
<i>trans</i> -[CrBr ₂ (en)(pn)]Br·2H ₂ O	5,5		<0 ^a	114	7
<i>trans</i> -[CrCl ₂ (en)(tn)]Cl·HCl·2H ₂ O	5,6		-13	181	7
<i>trans</i> -[CrBr ₂ (en)(tn)]Br·HBr·2H ₂ O	5,6		<0 ^a	123	7
<i>trans</i> -[CrCl ₂ (pn)(tn)]Cl·H ₂ O	5,6		<i>c</i>	<i>c</i>	7
<i>trans</i> -[CrBr ₂ (pn)(tn)]Br·HBr·2H ₂ O	5,6		<i>c</i>	<i>c</i>	7
Simple Bis(diamine) Complexes					
<i>cis</i> -[CrCl ₂ (tn) ₂]Cl·0.5H ₂ O	6,6	cis to trans	-21	163	5
<i>cis</i> -[CrBr ₂ (tn) ₂]Br·2H ₂ O	6,6		<0 ^a	215	6
<i>cis</i> -[CrCl ₂ (ptn) ₂]Cl·2H ₂ O (IX)	6,6		-59	155	

^a <0 designates the appearance of substantially exothermic DTA peaks. ^b The value was not obtained because of the lack of any suitable solvent. ^c The values were not obtained because of the occurrence of complicated decomposition during isomerization.

from green to violet, which is an indication of the occurrence of trans-to-cis isomerization.

Complex IX lost 2 mol of water at 30–155 °C and was decomposed above 300 °C. The complex turned to green from violet at 245 °C where the DTA curve shows an exothermic peak, which is due to cis-to-trans isomerization.

The enthalpy changes for dehydration and/or dehydrohalogenation were estimated from the DTA curves to be 63, 76, 38, and 29 kJ mol⁻¹ for complexes I, II, III, and IX. The enthalpy changes for isomerization are -42, -24, <0, and -59 kJ mol⁻¹ for complexes I, II, III, and IX (Table III).

Rate of Dehydration and/or Dehydrohalogenation. If the rates of dehydration and/or dehydrohalogenation at each temperature obey a 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 and/or dehydrohalogenated sample during time *t*, and *k_d* is the rate constant. Linear relationships were obtained when log [*a*/(*a* - *x*)] was plotted against time *t*. Table II contains *k_d* obtained from these relationships together with the rate constants of isomerization (*k_i*). From

the Arrhenius plots of *k_d*, the *E_d*'s for dehydration plus dehydrohalogenation of complexes I and II were estimated to be 92 and 101 kJ mol⁻¹. For complex III, the *E_d*'s for dehydrohalogenation and for dehydration were obtained as 92 and 118 kJ mol⁻¹, respectively. The dehydration stage of complex IX had an activation energy of 84 kJ mol⁻¹.

Rate of Isomerization. The isomerization of complexes II, III, and IX was traced spectrophotometrically. In a manner similar to that of dehydration, the values of log [*b*/(*b* - *y*)] were plotted against time *t*, where *b* is the initial amount of the complexes and *y* is the amount of the isomerized product. Linear relationships were obtained, indicating that the isomerization obeys a first-order law. The rate constants for isomerization (*k_i*) are given in Table II. The activation energies of isomerization were calculated to be 176, 163, and 155 kJ mol⁻¹ for complexes II, III, and IX, respectively (Table III). As for complex III, comparison of *k_d* with *k_i* at various temperatures (Table II) reveals that the isomerization starts at a lower temperature (200 °C) than the dehydration (210 °C): the former precedes the latter. The isomerization of complexes I and V could not be traced because a common solvent for the starting material, intermediate, and the final product could not be found.

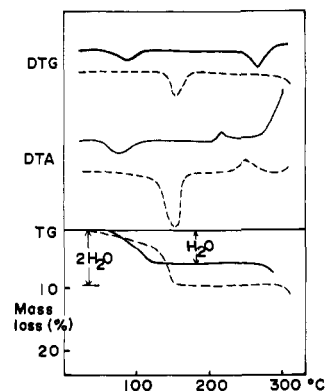


Figure 3. Derivatograms of complexes V (—) and IX (---).

Discussion

Relation between Dehydration and/or Dehydrohalogenation and Isomerization. Figure 4 presents the temperature ranges for dehydration and/or dehydrohalogenation and for isomerization of the present compounds and the other related simple and mixed bis(diamine) complexes. A glance at the figure tells us that the temperature ranges for isomerization are independent of those for dehydration and/or dehydrohalogenation for all the complexes except for *trans*-[CrCl₂(pn)₂]Cl·1.5H₂O, *trans*-[CrCl₂(chxn)₂]Cl·HCl·2H₂O (III), and *trans*-[CrBr₂(en)(pn)]Br·2H₂O. As mentioned in the previous section, complex III isomerizes prior to the dehydration stage. The situation is also true for *trans*-[CrCl₂(pn)₂]Cl·1.5H₂O.⁵ The isomerization of *trans*-[CrBr₂(en)(pn)]Br·2H₂O starts after the initiation of dehydration and finishes before the completion of dehydration. Accordingly, it may be concluded that the isomerization of the chromium(III) complexes takes place with no participation of water and/or hydrogen halide.

Direction of Isomerization. Table III summarizes the enthalpy changes (ΔH_i) and activation energies (E_i) for the isomerization of the present bis(diamine) complexes and the

other homologues. The table also contains the combination of members in chelate rings and the direction of isomerization. The compounds that have two five-membered chelate rings isomerize from *trans* to *cis* irrespective of the simple and mixed bis(diamine) complexes. On the other hand, *cis*-to-*trans* isomerization was recognized for the compounds containing two six-membered chelate rings. We expected at the beginning of the studies that the mixed bis(diamine) complexes having a combination of five- and six-membered chelate rings might undergo both *cis*-to-*trans* and *trans*-to-*cis* isomerization. However, the expectation did not come true: the isomerization was one way (*trans*-to-*cis*).

The ΔH_i values in Table III indicate that all the complexes isomerize exothermically except for *trans*-[CrCl₂(pn)(tn)]Cl·H₂O and *trans*-[CrBr₂(pn)(tn)]Br·HBr·2H₂O, where the DTA curves could not be analyzed because of complicated decomposition during isomerization.

Effect of Cl and Br Ions on Isomerization. Comparison of the E_i values in Table III shows a general trend in the isomerization of the chloro and the corresponding bromo complexes. In the case of the simple bis(diamine) complexes, the bromo complexes have greater activation energies (420 kJ mol⁻¹ for *trans*-[CrBr₂(en)₂]Br·H₂O and 215 kJ mol⁻¹ for *cis*-[CrBr₂(tn)₂]Br·2H₂O) than the chloro complexes (202 kJ mol⁻¹ for *trans*-[CrCl₂(en)₂]Cl·HCl·2H₂O and 163 kJ mol⁻¹ for *cis*-[CrCl₂(tn)₂]Cl·0.5H₂O). On the contrary, the chloro compounds in the mixed bis(diamine) complexes have greater activation energies (155 kJ mol⁻¹ for *trans*-[CrCl₂(en)(pn)]Cl·0.75H₂O and 181 kJ mol⁻¹ for *trans*-[CrCl₂(en)(tn)]Cl·HCl·2H₂O) than the bromo compounds (114 kJ mol⁻¹ for *trans*-[CrBr₂(en)(pn)]Br·2H₂O and 123 kJ mol⁻¹ for *trans*-[CrBr₂(en)(tn)]Br·HBr·2H₂O). This suggests that the chloro complexes isomerize more easily than the bromo complexes in the simple bis(diamine) complexes but that the reverse is true for the mixed bis(diamine) complexes. The reason is still unknown, further studies being needed to elucidate this.

Mechanism of Isomerization. Several workers have reported on the mechanism of the solid-phase racemization of metal

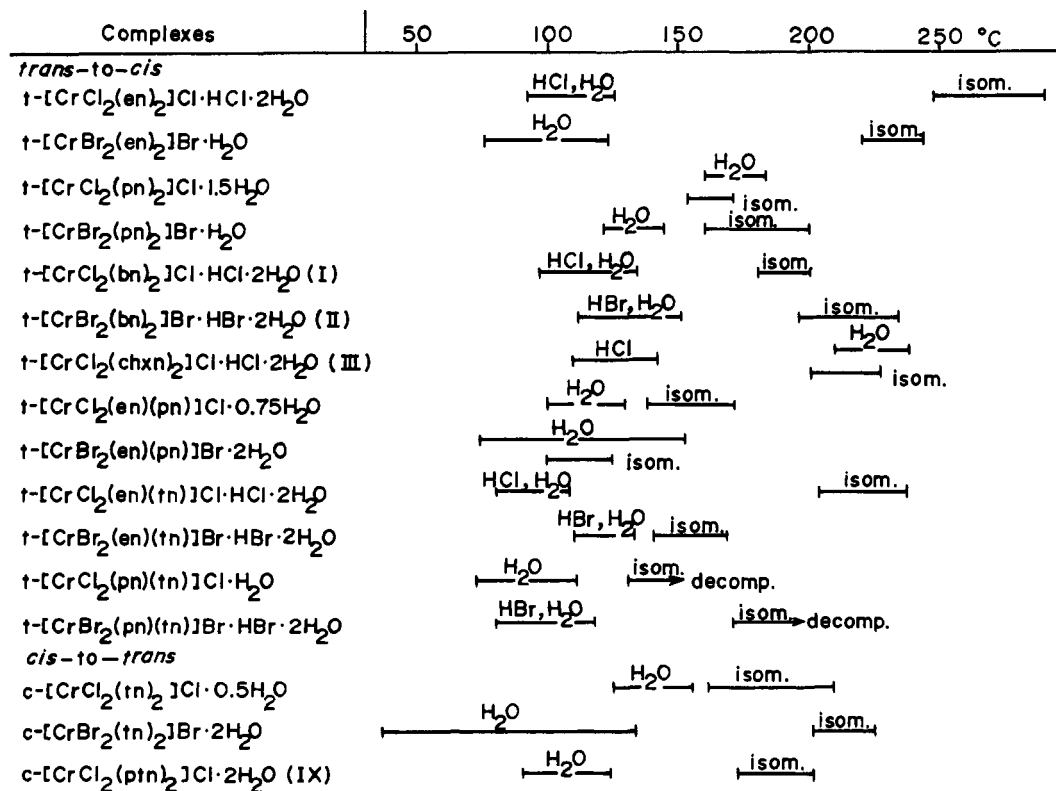


Figure 4. Temperature ranges for dehydration and/or dehydrohalogenation and for isomerization of the simple and mixed bis(diamine) complexes: HCl, H₂O, dehydrochlorination and dehydration; isom, isomerization; H₂O, dehydration; HBr, H₂O, dehydrobromination and dehydration; HCl, dehydrochlorination.

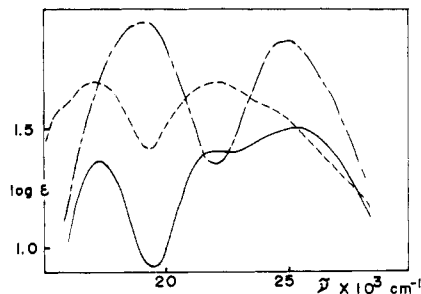


Figure 5. Electronic spectra of complex I (—) in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$, the intermediate X (---) in DMF, and complex VI (· · ·) in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$.

complexes: e.g., a twist mechanism is preferably accepted in the racemization of tris(oxalato)metalate,^{19,20} and LeMay and Bailar reported that the racemization of *l-cis*-[CrCl₂(en)₂]-Cl·H₂O proceeds via an aquation-anation mechanism.²¹ On the other hand, it has been found for the following cobalt(III) complexes that lattice water participates in the isomerization and intermolecular aquation-anation:¹¹ *trans*-[CoCl₂(NH₃)₄]IO₃·2H₂O,⁹ *trans*-[CoCl₂(pn)₂]Cl·HCl·2H₂O,^{8a,10} *trans*-[CoBr₂(pn)₂]Br·HBr·2H₂O,^{8c} and *cis,trans*-[CoCl₂(NH₃)₂(en)]Br·H₂O.^{8b}

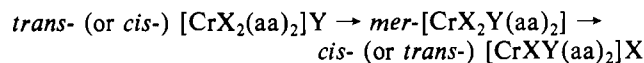
As mentioned above, the essential differences in the solid-phase isomerization between the cobalt(III) and chromium(III) complexes are that (1) the reaction of the chromium(III) complexes does not require the participation of lattice water and/or hydrogen halide and (2) the reaction of the chromium(III) complexes is in all cases exothermic. No participation of water and/or hydrogen halide may discard the intermolecular mechanism, and the exothermic reaction may not fit for an intermolecular twisting mechanism. An intramolecular bond-rupture process may therefore be predominant.

In this study, we succeeded in isolating the intermediate X (*mer*-[CrCl₂(bn)₂]·H₂O) during the isomerization of complex I (*trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O), the intermediate X, and complex VI (*cis*-[CrCl₂(bn)₂]Cl·H₂O). As seen from the figure, the *trans* complex has, as expected, three absorption bands in the range of the d-d transition [$17.2 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 1.38$), $22.2 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 1.39$), and $25.2 \times 10^3 \text{ cm}^{-1}$

($\log \epsilon = 1.50$)] and the *cis* complex has two bands [$18.9 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 1.90$) and $24.9 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 1.87$)]. On the other hand, the intermediate X has bands at $17.0 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 1.70$) and $22.0 \times 10^3 \text{ cm}^{-1}$ ($\log \epsilon = 1.70$); inspection of the spectrum reveals that appreciable shoulders are detectable near 15.6×10^3 and $24.5 \times 10^3 \text{ cm}^{-1}$. The appearance of these shoulders may, as has been reported in studies on [CrCl₃(dien)],²² [CoCl₃(diene)],²² and [CoCl₃(N-H₃)₃],²³ suggest that three chloride ions are coordinated in a *mer* position.

Additionally, it was found that the product obtained in the isomerization of complex V (*trans*-[CrCl₂(bn)₂]Br·H₂O) is *cis*-[CrBrCl(bn)₂]Cl and not *cis*-[CrCl₂(bn)₂]Br. This is supported by the facts that (i) the molar conductivity of the product in $10^{-3} \text{ mol dm}^{-3}$ methanol is $86.5 \Omega^{-1} \text{ cm}^2$, indicating that it is a 1:1 type electrolyte and (ii) the second band in the electronic spectrum of the product appears at $24.8 \times 10^3 \text{ cm}^{-1}$, which lies just in between $24.5 \times 10^3 \text{ cm}^{-1}$ for complex VI (*cis*-[CrCl₂(bn)₂]Cl·H₂O) and $25.1 \times 10^3 \text{ cm}^{-1}$ for complex VII (*cis*-[CrBr₂(bn)₂]Br·3H₂O). On the other hand, *mer*-[CrBr₃(en)(pn)]·2H₂O and *mer*-[CrBr₃(pn)(tn)]·2H₂O have also been isolated during the isomerization of *trans*-[CrBr₂(en)(pn)]Br·2H₂O and *trans*-[CrBr₂(pn)(tn)]Br·HBr·2H₂O, respectively.⁶

From these results, it is reasonably concluded that the isomerization of the chromium(III) complexes proceeds through a bond-rupture pathway as shown:



where X and Y designate chloride and/or bromide ions, aa is diamine, and one of two diamines in the intermediate is coordinated unidentate to chromium(III) ion.

Registry No. *trans*-[CrCl₂(bn)₂]Cl·HCl, 79839-79-5; *trans*-[CrBr₂(bn)₂]Br·HBr, 79839-78-4; *trans*-[CrCl₂(chxn)₂]Cl·HCl, 79980-86-2; *trans*-[CrCl₂(ptn)₂]Cl·HCl, 79980-84-0; *trans*-[CrCl₂(bn)₂]Br, 79840-44-1; *cis*-[CrCl₂(bn)₂]Cl, 79840-45-2; *cis*-[CrBr₂(bn)₂]Br, 79897-18-0; *cis*-[CrCl₂(chxn)₂]Cl, 79896-42-7; *cis*-[CrCl₂(ptn)₂]Cl, 79896-48-3; *mer*-[CrCl₃(bn)₂], 62987-96-6; *trans*-[CrF₂(bn)₂]ClO₄, 79840-47-4; *trans*-[CrF₂(chxn)₂]ClO₄, 79896-41-6; *trans*-[CrF₂(ptn)₂]ClO₄, 79896-50-7.

Supplementary Material Available: Table I listing analytical data (1 page). Ordering information is given on any current masthead page.

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