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THERMAL *CIS—TRANS* ISOMERIZATION OF BIS(DIAMINE) COBALT(III) AND CHROMIUM(III) COMPLEXES IN A SOLID PHASE

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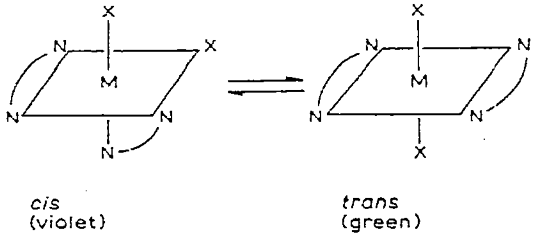
ABSTRACT

Thermal *cis—trans* isomerization of the simple bis(diamine) complexes $[MX_2(\text{aa or bb})_2]X \cdot HX \cdot n\,H_2O$ and the mixed bis(diamine) complexes $[MX_2(\text{aa})(\text{bb})]X \cdot HX \cdot n\,H_2O$ was investigated in a solid phase, where M = Co(III) or Cr(III) ion, X = Cl or Br, aa and bb are one of the diamines selected from ethylenediamine (en), *d,l*-1,2-propanediamine (pn), *d,l*-2,3-butanediamine (*dl*-bn), *d,l*-1,2-cyclohexanediamine (chxn), 1,3-propanediamine (tn) and *d,l*-2,4-pentanediamine (ptn), and $n = 0$—2. The information obtained may be summarized as follows. (1) The features of isomerization are considerably dependent upon the kind of metal ions, halide ions and diamines contained in the complexes. (2) *Trans—cis* isomerization was identified in the simple bis(diamine) complexes containing en, pn, *dl*-bn or chxn which can form five-membered chelate rings with metal ions, whereas *cis—trans* isomerization was detected in the simple bis(diamine) complexes containing tn or ptn which forms six-membered rings; all the mixed bis(diamine) complexes isomerize from *trans* to *cis* even when they have a combination of five- and six-membered chelate rings. (3) The cobalt(III) complexes isomerize in a temperature range of dehydration and/or dehydrohalogenation with activation energies of about 100 kJ mole^{-1}, whereas the chromium(III) complexes usually isomerize in the anhydrous state and the activation energies amount to as much as 150—190 kJ mole^{-1}. (4) "Aquation—anation" and "bond rupture" were proposed for the isomerization of the cobalt(III) and the chromium(III) complexes, respectively.

INTRODUCTION

Extensive studies have been carried out on the *cis—trans* isomerization of octahedral bis(diamine) metal complexes in solution [1] which are depicted in the scheme



where M is the metal ion, X is the halide or pseudo-halide ion, and N—N is the diamine. On the other hand, several structural changes of some metal complexes are known to take place in a solid phase before they undergo a complicated decomposition. Among them, *cis—trans* isomerization in a solid phase is the most conspicuous reaction as in a solution. The reaction in a solid phase has, however, been treated in a few papers, which are exemplified as follows

trans-$[CoCl_2(NH_3)_4]IO_3 \cdot 2\ H_2O(s)$

$\rightarrow$ *cis*-$[CoCl_2(NH_3)_4]IO_3(s) + 2\ H_2O(g)$ [2,3]

cis,trans-$[CoCl_2(NH_3)_2en]Br \cdot H_2O(s)$

$\rightarrow$ *trans,cis*-$[CoCl_2(NH_3)_2en]Br(s) + H_2O(g)$ [4]

cis,trans-$[CoCl_2(NH_3)_2en]SCN \cdot H_2O(s)$

$\rightarrow$ *cis,cis*-$[CoCl(NCS)(NH_3)_2en]\ Cl(s) + H_2O(g)$ [5]

The present paper deals with details of the *cis—trans* isomerization of the simple bis(diamine) complexes $[MX_2(aa\ or\ bb)]X \cdot HX \cdot n\ H_2O$ and the mixed bis(diamine) complexes $[MX_2(aa)(bb)]X \cdot HX \cdot n\ H_2O$ in a solid phase, where M = Co(III) or Cr(III) ion, X = Cl or Br, aa and bb are diamines selected from ethylenediamine (en), *d,l*-1,2-propanediamine (pn), *d,l*-2,3-butanediamine (*dl*-bn), *d,l*-1,2-cyclohexanediamine (chxn), 1,3-propanediamine (tn) and *d,l*-2,4-pentanediamine (ptn); and $n = 0$—2.

EXPERIMENTAL

Preparation of complexes

The diamines used in the preparation of the complexes are en, pn, *dl*-bn, chxn, tn and ptn. The following complexes were prepared as described in the literature or by modification of the usual methods: *trans*-$[CoCl_2en_2]Cl \cdot HCl \cdot 2\ H_2O$ [6], *cis*-$[CoCl_2en_2]Cl$ [7], *trans*-$[CoCl_2pn_2]Cl \cdot HCl \cdot 2\ H_2O$ [8], *cis*-$[CoCl_2pn_2]Cl$ [9], *trans*-$[CoBr_2pn_2]Br \cdot HBr \cdot 2\ H_2O$ [10], *cis*-$[CoBr_2pn_2]Br$ [10], *trans*-$[CoCl_2tn_2]Cl$ [11], *cis*-$[CoCl_2tn_2]Cl \cdot DMSO \cdot 2\ H_2O$ [12], *trans*-$[CrCl_2en_2]Cl \cdot HCl \cdot 2\ H_2O$ [13], *cis*-$[CrCl_2en_2]Cl$ [14], *trans*-$[CrBr_2en_2]Br \cdot H_2O$ [15], *cis*-$[CrBr_2en_2]Br \cdot H_2O$ [16], *trans*-$[CrCl_2pn_2]Cl \cdot 1.5\ H_2O$ [17], *cis*-$[CrCl_2pn_2]Cl$ [18], *trans*-$[CrBr_2pn_2]Br \cdot H_2O$ [19], *cis*-$[CrBr_2pn_2]Br$ [19], *trans*-$[CrCl_2enpn]Cl \cdot 0.75\ H_2O$ [20], *cis*-$[CrCl_2enpn]Cl$ [20], *trans*-$[CrCl_2entn]Cl \cdot HCl \cdot 2\ H_2O$ [20], *cis*-$[CrCl_2entn]Cl$ [20], *trans*-$[CrCl_2pntn]Cl \cdot H_2O$ [20], *trans*-$[CrBr_2enpn]Br \cdot 2\ H_2O$ [20], *cis*-$[CrBr_2enpn]Br \cdot 2\ H_2O$ [20], *trans*-$[CrBr_2entn]Br \cdot HBr \cdot 2\ H_2O$ [20], *trans*-$[CrBr_2pntn]Br \cdot HBr \cdot 2\ H_2O$ [20], *cis*-$[CrBr_2pntn]Br \cdot H_2O$ [20], *trans*-$[CrCl_2(dl\text{-}bn)_2]Cl \cdot HCl \cdot 2\ H_2O$ [21], *cis*-$[CrCl_2(dl\text{-}bn)_2]Cl$ [21], *trans*-$[CrBr_2(dl\text{-}bn)_2]Br \cdot HBr \cdot 2\ H_2O$ [21], *cis*-$[CrBr_2(dl\text{-}bn)_2]Br$ [21], *trans*-$[CrCl_2(chxn)_2]Cl \cdot HCl \cdot 2\ H_2O$ [15], *cis*-$[CrCl_2(chxn)_2]Cl \cdot 2\ H_2O$ [13], *trans*-$[CrCl_2tn_2]Cl$ [13], *cis*-$[CrCl_2tn_2]Cl \cdot 0.5\ H_2O$ [13], *trans*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ [22], *cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ [16], *trans*-$[CrCl_2(ptn)_2]Cl \cdot HCl \cdot 2\ H_2O$ [13], and *cis*-$[CrCl_2(ptn)_2]Cl \cdot 2\ H_2O$ [13].

Identification of mixed-diamine complexes

Thin layer chromatography (TLC) was sufficiently powerful to distinguish the mixed bis(diamine) complexes $[CrX_2(aa)(bb)]X$ from the mixture of the simple bis(diamine) complexes, $[CrX_2(aa)_2]X$ and $[CrX_2(bb)_2]X$. Silica gel 60F-254 plates (Merck Ltd.) were used fo TLC. The R_f values fo $[CrX_2(aa)(bb)]X$ were between those for $[CrX_2(aa)_2]X$ and $[CrX_2(bb)_2]X$, indicating that the desired mixed bis(diamine) complexes were successfully obtained [20].

Isothermal measurements

The rates of dehydration and/or dehydrohalogenation of the complexe were measured from weight changes using a Chyo 1001 thermobalance. Th rates of isomerization were determined by measuring the absorbances of th samples heated in an Abderhalden apparatus or on an Ikemoto Rika Kogy air bath at each desired temperature and the isomerization ratios were calculated by solving the simultaneous equations containing the molar extinction coefficients of the *cis*- and *trans*-form complexes.

RESULTS AND DISCUSSION

The rate constants for the dehydration and/or dehydrohalogenation, k_d and for the isomerization, k_i, are summarized in Table 1. Of the complexe dealt with in this paper, complexes I, II, and IV—XVI were found to isomerize from *trans* to *cis*, whereas complexes, III, XVII, XVIII and XIX isomerized from *cis* to *trans*.

Referring to the data in Table 1, a striking difference is found between th cobalt(III) and chromium(III) complexes, viz., the cobalt(III) complexe isomerize along with the dehydration and/or dehydrohalogenation (or evolution of DMSO), while the chromium(III) complexes, except (VI) *trans*-$[CrCl_2pn_2]Cl \cdot 1.5\ H_2O$, (XI) *trans*-$[CrBr_2enpn]Br \cdot 2\ H_2O$ and (XVI) *trans*-$[CrCl_2(chxn)_2]Cl \cdot HCl \cdot 2\ H_2O$, isomerize in an anhydrous state at relativel higher temperatures after the complete liberation of lattice water and/o

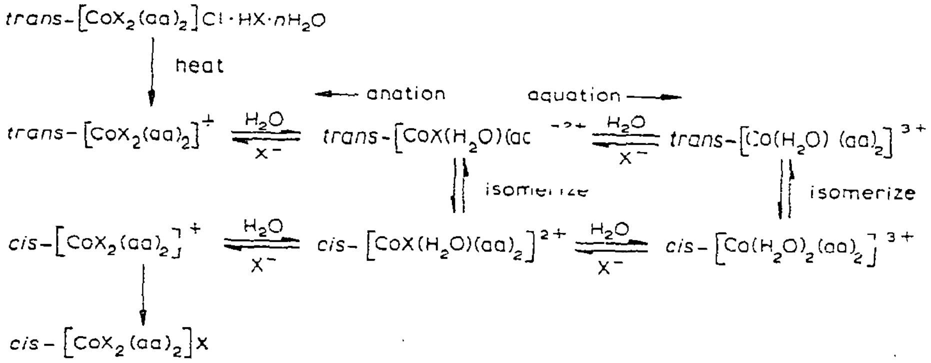


Fig. 1. Scheme for the "aquation—anation" mechanism in isomerization.

TABLE 1

Rate constants for dehydration and/or dehydrohalogenation, k_d, and isomerization, k_i

(I) *trans*-[$CoCl_2pn_2$]Cl · HCl · 2 H_2O					
t(°C)	110	120	130	140	150
$k_d \times 10^4$ (s^{-1})	2.6	4.3	8.2	12	16
$k_i \times 10^4$ (s^{-1})	0.44	1.2	1.8	3.8	7.3
(II) *trans*-[$CoBr_2pn_2$]Br · HBr · 2 H_2O					
t(°C)	90	98	100	110	111
$k_d \times 10^4$ (s^{-1})	0.36	0.60		2.5	
$k_i \times 10^4$ (s^{-1})			0.28		0.78
(III) *cis*-[$CoCl_2tn_2$]Cl · DMSO · 2 H_2O					
t(°C)	110	120	130	140	
$k_d \times 10^4$ (s^{-1})	1.94	2.78	3.98	5.32	
$k_i \times 10^3$ (s^{-1})	0.691	2.28	18.9	46.1	
(IV) *trans*-[$CrCl_2en_2$]Cl · HCl · 2 H_2O					
t(°C)	92.0	105.0	119.3	125.5	240
k_d(HCl) $\times 10^3$ (s^{-1})	0.642	1.075	2.084	2.572	
k_d(H_2O) $\times 10^3$ (s^{-1})	1.574	2.764	3.964	4.798	
$k_i \times 10^4$ (s^{-1})					1.151
(V) *trans*-[$CrBr_2en_2$]Br H_2O					
t(°C)	75	81	90	98	107
$k_d \times 10^4$ (s^{-1})	0.96	3.07	3.95	6.20	9.74
$k_i \times 10^4$ (s^{-1})					
(VI) *trans*-[$CrCl_2pn_2$]Cl · 1.5 H_2O					
t(°C)	154	160	166	172	178
$k_d \times 10^4$ (s^{-1})		3.009		5.322	7.043
$k_i \times 10^2$ (s^{-1})	1.490	3.133	6.821	13.08	
(VII) *trans*-[$CrBr_2pn_2$]Br · H_2O					
t(°C)	122	127	138	146	160
$k_d \times 10^4$ (s^{-1})	7.3	8.8	23	35	
$k_i \times 10^5$ (s^{-1})					0.31
(VIII) *trans*-[$CrCl_2$enpn]Cl · 0.75 H_2O					
t(°C)	100	109	120	130	138
$k_d \times 10^4$ (s^{-1})	4.27	7.48	12.7	21.7	
$k_i \times 10^4$ (s^{-1})					0.24
(IX) *trans*-[$CrCl_2$entn]Cl · HCl · 2 H_2O					
t(°C)	80	87	99	108	205
$k_d \times 10^4$ (s^{-1})	6.73	9.60	17.6	25.6	
$k_i \times 10^4$ (s^{-1})					0.81
(X) *trans*-[$CrCl_2$pntn]Cl · H_2O					
t(°C)	73	86	94	103	113
$k_d \times 10^4$ (s^{-1})	1.92	4.99	9.21	13.3	26.9
(XI) *trans*-[$CrBr_2$enpn]Br · 2 H_2O					
t(°C)	70	78	89	100	108
$k_d \times 10^4$ (s^{-1})	2.56	4.67	5.76	9.12	
$k_i \times 10^4$ (s^{-1})				0.96	1.66

160	170	180	190			
19	24	33	41			
13	24	33	41			
117	130					
40						
1.7	5.5					
(Dehydration and evolution of DMSO)						
260	269	279	288			
(Dehydrochlorination)						
(Dehydration)						
2.955	5.245	16.97	29.17			
220	225	230	235	240		
0.10	0.26	0.94	2.29	6.12		
184						
9.135						
170	180	190	200			
1.4	2.9	8.8	23			
153	159	172				
1.22	2.22	7.70				
214	222	238				
1.95	3.95	15.3				
111	116.5	125	130	138	146	153
			8.47	13.9	26.6	44.1
2.88	4.80	10.4				

TABLE 1 (continued)

(XII) *trans*-[CrBr$_2$entn]Br · HBr · 2 H$_2$O					
t(°C)	80	89	100	110	118
$k_d \times 10^4$ (s^{-1})	3.22	4.32	5.28	6.97	9.90
(XIII) *trans*-[CrBr$_2$pntn]Br · HBr · 2 H$_2$O					
t(°C)	110	115	120	126	133
$k_d \times 10^4$ (s^{-1})	0.55	0.84	1.42	2.24	3.99
$k_i \times 10^4$ (s^{-1})					
(XIV) *trans*-[CrCl$_2$(*dl*-bn)$_2$]Cl · HCl · 2 H$_2$O					
t(°C)	97	110	119	131	136
$k_d \times 10^4$ (s^{-1})	1.55	4.30	9.21	19	25.3
(XV) *trans*-[CrBr$_2$(*dl*-bn)$_2$]Br · HBr · 2 H$_2$O					
t(°C)	112	120	133	141	151
$k_d \times 10^3$ (s^{-1})	0.496	0.933	2.510	4.677	9.550
$k_i \times 10^4$ (s^{-1})					
(XVI) *trans*-[CrCl$_2$(chxn)$_2$]Cl · HCl · 2 H$_2$O					
t(°C)	111	121	128	135	143
k_d(HCl) × 10^3 (s^{-1})	0.430	0.871	1.545	2.375	3.980
k_d(H$_2$O) × 10^3 (s^{-1})					(Dehydration)
$k_i \times 10^3$ (s^{-1})					
(XVII) *cis*-[CrCl$_2$tn$_2$]Cl · 0.5 H$_2$O					
t(°C)	129	136	144	155	160
$k_d \times 10^3$ (s^{-1})	2.46	2.79	3.69	4.98	
$k_i \times 10^4$ (s^{-1})					0.140
(XVIII) *cis*-[CrBr$_2$tn$_2$]Br · 2 H$_2$O					
t(°C)	67	76	85	94	200
$k_d \times 10^4$ (s^{-1})	8.53	10.87	18.05	28.99	
$k_i \times 10^4$ (s^{-1})					0.27
(XIX) *cis*-[CrCl$_2$(ptn)$_2$]Cl · 2 H$_2$O					
t(°C)	91	100	108	123	172
$k_d \times 10^3$ (s^{-1})	1.063	1.560	2.221	4.054	
$k_i \times 10^4$ (s^{-1})					0.741

hydrogen halide. The isomerization of complexes VI and XVI precedes dehydration. Complex XI isomerizes together with the dehydration, but the reaction is exothermic. This implies the difference that exists in isomerization mechanism between cobalt(III) and chromium(III) complexes.

The mechanism in the *trans*–*cis* isomerization of cobalt(III) complexes in polar solvents has been interpreted as a solvation–anation reaction [23a, b]. It was pointed out that the isomerization with dehydration and dehydrochlorination in *trans*-[CoCl$_2$pn$_2$]Cl · HCl · 2 H$_2$O in a solid phase takes place by an "aquation–anation" mechanism, as in an aqueous solution [3,24]. Other cobalt(III) complexes are also considered to isomerize via this mechanism which is schematized in Fig. 1.

138	151	156	161	168			
0.56	1.41	2.52	4.08	7.20			
195	203	210	224	236			
0.398	0.861	1.318	6.025	15.35			
200	209	210	222	223	229	231	240
(Dehydrochlorination)							
0.590	1.380	1.470	2.818	4.467	6.540	4.731	8.105
170	181	190	199	209			
0.356	1.044	2.252	5.911	12.60			
209	218	225					
0.53	1.78	5.02					
179	192	201					
1.375	4.222	9.26					

In this mechanism, as shown in Fig. 1, the isomerization path involves the formation of aqua- and diaqua-complexes in the intermediates. It is therefore easily understood by this mechanism that the participation of lattice water is required to make the cobalt(III) complexes isomerize. On the other hand, the isomerization of chromium(III) complexes is considered to proceed in a way different to that of cobalt(III) complexes, because the isomerization does not, in general, require the participation of lattice water. In addition, the isomerization proceeds exothermically in all the chromium(III) complexes studied in this work. Furthermore, the intermediates, *mer*-$[CrCl_3(bn)_2] \cdot H_2O$, *mer*-$[CrBr_3(en)(pn)] \cdot 2\,H_2O$ and *mer*-$[CrBr_3(pn)(tn)] \cdot 2\,H_2O$ were isolated during the isomerization of *trans*-$[CrCl_2(bn)_2]Cl \cdot HCl \cdot$

TABLE 2

Survey of isomerization in $[MX_2(aa)_2]X \cdot HX \cdot n\ H_2O$ type complexes

Complexes		E_d (kJ mole^{-1})	E_i (kJ mole^{-1})	Ref.
(I)	*trans*-$[CoCl_2pn_2]Cl \cdot HCl \cdot 2\ H_2O$	42	96	26
(II)	*trans*-$[CoBr_2pn_2]Br \cdot HBr \cdot 2\ H_2O$	117	117	10
(III)	*cis*-$[CoCl_2tn_2]Cl \cdot DMSO \cdot 2\ H_2O$	48	184	12
(IV)	*trans*-$[CrCl_2en_2]Cl \cdot HCl \cdot 2\ H_2O$	118 (HCl) * 42 (H_2O) **	202	27
(V)	*trans*-$[CrBr_2en_2]Br \cdot H_2O$	61	420	28
(VI)	*trans*-$[CrCl_2pn_2]Cl \cdot 1.5\ H_2O$	76	193	27
(VII)	*trans*-$[CrBr_2pn_2]Br \cdot H_2O$	96	180	19
(VIII)	*trans*-$[CrCl_2enpn]Cl \cdot 0.75\ H_2O$	67	155	20
(IX)	*trans*-$[CrCl_2entn]Cl \cdot HCl \cdot 2\ H_2O$	55	181	20
(X)	*trans*-$[CrCl_2pntn]Cl \cdot H_2O$	76		20
(XI)	*trans*-$[CrBr_2enpn]Br \cdot 2\ H_2O$	46 (1st step) 103 (2nd step)	114	20
(XII)	*trans*-$[CrBr_2entn]Br \cdot HBr \cdot 2\ H_2O$	30		20
(XIII)	*trans*-$[CrBr_2pntn]Br \cdot HBr \cdot 2\ H_2O$	112	123	20
(XIV)	*trans*-$[CrCl_2(dl\text{-}bn)_2]Cl \cdot HCl \cdot 2\ H_2O$	92		21
(XV)	*trans*-$[CrBr_2(dl\text{-}bn)_2]Br \cdot HBr \cdot 2\ H_2O$	101	176	21
(XVI	*trans*-$[CrCl_2(chxn)_2]Cl \cdot HCl \cdot 2\ H_2O$	92 (HCl) * 118 (H_2O) **	163	21
(XVII)	*cis*-$[CrCl_2tn_2]Cl \cdot 0.5\ H_2O$	42	163	29
(XVIII)	*cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$	38	215	28
(XIX)	*cis*-$[CrCl_2(ptn)_2]Cl \cdot 2\ H_2O$	84	155	21

* Dehydrochlorination step.

** Dehydration step.

$2\ H_2O$, *trans*-$[CrBr_2(en)(pn)]Br \cdot 2\ H_2O$ and *trans*-$[CrBr_2(pn)(tn)]Br \cdot HBr \cdot 2\ H_2O$, respectively [20,25]. From these facts, the "bond rupture" mechanism is proposed to be operative in the isomerization of the chromium(III) complexes, which is schematically represented in Fig. 2. As is seen in Fig. 2, one of the diamines in the intermediates functions as unidentate and their formation was verified by measuring their absorption spectra.

From the Arrhenius plots of the rate constants for dehydration and/or dehydrohalogenation (or evolution of DMSO) and for isomerization listed in Table 1, the activation energies for the respective reactions, E_d and E_i, were calculated and are summarized in Table 2. *Trans*-$[CoCl_2en_2]Cl \cdot HCl \cdot 2$

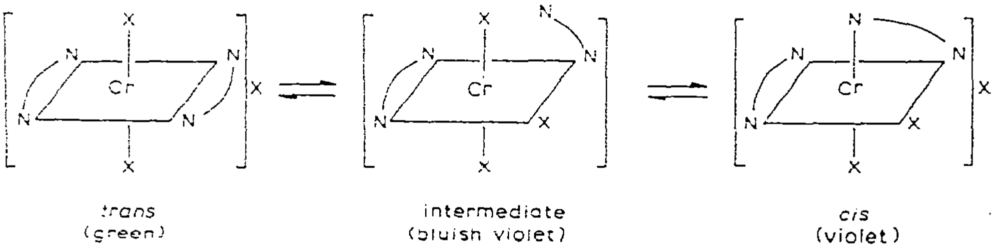


Fig. 2. Scheme for the "bond rupture" mechanism in isomerization.

TABLE 3

The dependence of activation energy on the diamine contained in the complex

Dichloro-complexes		E_i (kJ mole^{-1})	Dibromo-complexes		E_i (kJ mole^{-1})
IV	*trans*-[$CrCl_2en_2$]Cl · HCl · 2 H_2O	202	V	*trans*-[$CrBr_2en_2$]Br · H_2O	420
VI	*trans*-[$CrCl_2pn_2$]Cl · 1.5 H_2O	193	VII	*trans*-[$CrBr_2pn_2$]Br · H_2O	180
XVI	*trans*-[$CrCl_2(chxn)_2$]Cl · HCl · 2 H_2O	163	XV	*trans*-[$CrBr_2$(*dl*-bn)$_2$]Br · HBr · 2 H_2O	176

H_2O is not included in Table 2 since it does not isomerize to the corresponding *cis* complex in a solid phase and vice versa.

Inspection of Tables 1 and 2 gives the additional interesting information.

(1) The activation energies of isomerization are higher, at least in chromium(III) complexes VI and VII, than those in the corresponding cobalt(III) complexes I and II, and the temperature ranges where the isomerization takes place are, in general, higher in the chromium(III) complexes than in the corresponding cobalt(III) complexes (shown in Table 1). These facts indicate that the chromium(III) complexes are more difficult to isomerize than the cobalt(III) complexes. In addition, the activation energies for isomerization are much larger than those for dehydration and/or dehydrohalogenation in chromium(III) complexes, which also support involvement of the bond rupture mechanism in the isomerization of chromium(III) complexes, as mentioned above.

(2) So far as the simple bis(diamine) complexes I, II, V, XVII and XVIII are concerned, the dibromo-complexes have higher activation energies of isomerization than the corresponding dichloro-complexes. This shows that the presence of the bromide ion in a coordination sphere or as a counter-ion may give a slightly larger resistance to isomerization than that of the chloride ion.

(3) The activation energies for isomerization in dichloro-complexes IV, V and XVI and in dibromo-complexes V, VII and XV are given in Table 3. In both series of dichloro- and dibromo-complexes, the activation energies become smaller in the order of complexes containing en > pn > chxn and en > pn > *dl*-bn, respectively. Although the reason is not clear, these orders are coincident with those of the increased number of substituted $-CH_3$ groups.

(4) All the complexes studied in this work are classified into three groups in relation to the direction of isomerization, i.e., whether it occurs from *trans* to *cis* or from *cis* to *trans*. The first group includes complexes I, II, IV—VII and XIV—XVI. Complexes III, XVII, XVIII and XIX are included in the second group. The first group shows *trans—cis* isomerization, while the second group indicates *cis—trans* isomerization. The former group contains en, pn, *dl*-bn or chxn, and forms five-membered chelate rings with metal ions, whereas the latter contains tn or ptn and forms six-membered chelate rings.

The third group consists of the mixed bis(diamine) complexes VIII—XIII. The isomerization of this group is particularly interesting. We first expected the mixed bis(diamine) complexes having the combination of five- and six-membered chelate rings to undergo both *trans—cis* and *cis—trans* isomerization. This was based on the fact that, as mentioned above, only *trans—cis* isomerization was recognized in the simple bis(diamine) complexes $[CrX_2en_2$ (or pn_2, $bn_2)]X$, where en, pn or bn form five-membered chelate rings whereas only *cis—trans* isomerization was detected in the complexes $[CrX_2tn_2$ (or $ptn_2)]X$, in which tn and ptn form six-membered chelate rings. The expectation did not, however, come true. The isomerization was always one-way (*trans—cis*), even when the complexes contained five- and six-membered chelate rings simultaneously.

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