April, 1977]　BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (4), 883—885 (1977)　883

Derivatographic Studies on Transition Metal Complexes. XVIII.[1) Thermal Isomerization of *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$ in Solid Phase[2)

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(Received July 14, 1976)

The thermal *cis*-to-*trans* isomerization of *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$ in a solid phase was studied by means of derivatographic and isothermal measurements. It was found that *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$ in which trimethylenediamine(tn) forms six-membered chelate ring with chromium undergoes isomerization to the *trans*-complex in contrast with the isomerization of *trans*-$[MX_2(diam)_2]X \cdot HX \cdot nH_2O$ (M=Co or Cr, X=halogen) to the *cis*-one in which the diamine (diam) forms five-membered chelate ring with metal M. The isomerization proceeded in anhydrous state. The activation energy of the isomerization of the complex was found to be 163 kJ mol^{-1} from the isothermal measurements, which is fairly greater than that of the *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and *cis*-$[CoCl_2tn_2]Cl \cdot H_2O$. The difference was explained by whether or not water molecule involved as a lattice water contributes to the isomerization.

The thermal *trans*-to-*cis* isomerization of the transition metal complexes in a solid phase was reported for the dihalogenobis(diamine) series, *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$,[3),4) *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$,[5) *trans*-$[CrCl_2en_2]Cl$[6), and *trans*-$[CrBr_2pn_2]Br \cdot H_2O$.[7) In these complexes of the type $[MX_2(diam)_2]X \cdot HX \cdot nH_2O$, the modes of isomerization are influenced more or less by the kind of metal ion, M, halide ion, X, and diamine (diam). In the complex, *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, most part of the isomerization was reported to proceed simultaneously with dehydration and dehalogenation, the process being considered to follow an "aquation-anation" mechanism.[4) However, in the complex where the chloride ion is replaced by the bromide ion, *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$, the ratio of isomerization was 55% at the most, no isomerization proceeding after the dehydration was complete.[5)

On the other hand, in the case of the corresponding chromium(III) complex, *trans*-$[CrBr_2pn_2]Br \cdot H_2O$, dehydration was complete rapidly, isomerization successively proceeding even after complete dehydration.[7)

So far as the three complexes are concerned, isomerization occurred in the presence of water molecules involved in the cobalt(III) complexes, whereas it took place mainly in anhydrous state in the chromium(III) complexes. Although the cobalt(III) and chromium(III) complexes containing propylenediamine which forms a five-membered chelate ring with metal undergoes the *trans*-to-*cis* isomerization, it might be of interest to study type of isomerization appearing in the complexes containing trimethylenediamine which forms a six-membered chelate ring.

The present work was undertaken to investigate the kinetics of the isomerization of *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$, with the purpose of comparing its mode of isomerization with the modes of the corresponding cobalt(III) and propylenediamine complexes.

Experimental

Preparation of Complexes. Dichlorobis(trimethylenediamine)chromium(III) chlorides, *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$, and *trans*$[CrCl_2tn_2]Cl$, were prepared by a modification of the methods reported.[8) The chemical formulas of these compounds were confirmed by elemental analysis and spectrophotometric measurement.

Found: C, 22.82; H, 6.81; N, 17.76%. Calcd for *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$: C, 22.84; H, 6.71; N, 17.76%. Found: C, 23.73; H, 6.68; N, 18.28%. Calcd for *trans*-$[CrCl_2tn_2]Cl$: C, 23.51; H, 6.58; N, 18.28%.

Derivatography. The derivatogram for the complex *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$ was obtained with a MOM Typ-OD-102 Derivatograph. 0.5 g of the sample was used in each run under a constant flow of nitrogen with a heating rate of 1 °C min^{-1}. The activation energy was estimated by analysis of the DTA peak in a manner similar to that reported.[9)

Isothermal Measurements. The rate of dehydration of *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$ was measured at 129, 136, 144, and 155 °C with a CHO 100L thermobalance. 0.3 g of the sample in each run was heated at the desired temperature. The rate of dehydration was determined from the loss in mass of each sample in a constant time interval at each temperature, and the activation energy was calculated by means of the Arrhenius plots.

The rates of isomerization at 160, 170, 181, 190, 199, and 209 °C were followed by measuring the changes in absorbancy on the basis of the following equations similar to those report-

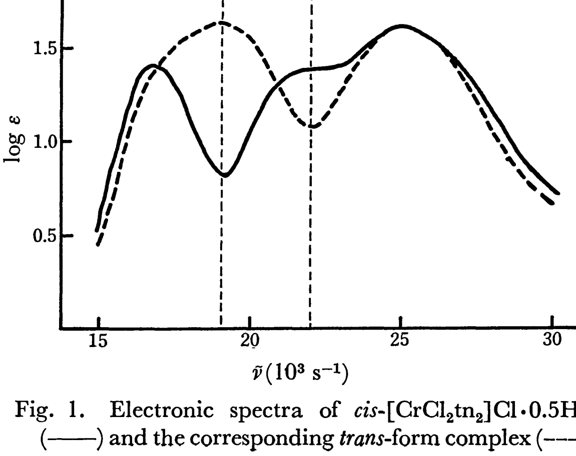


Fig. 1. Electronic spectra of *cis*-$[CrCl_2tn_2]Cl \cdot 0.5H_2O$ (——) and the corresponding *trans*-form complex (----).

ed.7)

$$5.87X + 46.10Y = D_{525}$$

$$23.98X + 12.00Y = D_{455},$$

where 5.87 and 23.98 are the molar extinction coefficients of the *cis*-complex, and 46.10 and 12.00 are those of the corresponding *trans* complex at 525 and 455 nm, respectively. The electronic spectra of the *cis* and *trans* complexes are shown in Fig. 1.

Results and Discussion

Derivatography. The derivatogram of *cis*-$[CrCl_2tn_2]Cl\cdot0.5H_2O$ is given in Fig. 2. The TG curve shows that the mass loss corresponding to the liberation of a half mole of water appears at 160 °C, followed by the presence of a plateau from 160 to 220 °C, the decomposition of complex then taking place rapidly.

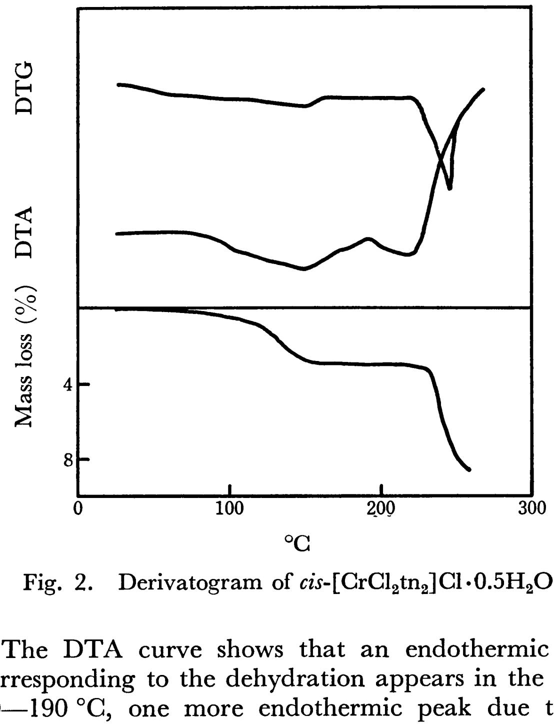


Fig. 2. Derivatogram of *cis*-$[CrCl_2tn_2]Cl\cdot0.5H_2O$.

The DTA curve shows that an endothermic peak corresponding to the dehydration appears in the range 70—190 °C, one more endothermic peak due to the isomerization appearing at 200—225 °C before an exothermic decomposition reaction begins. The isomerization from *cis*- to *trans*-form could be detected to occur at the second endothermic peak by the color change of the sample from violet to green.

The results indicate that the isomerization of the complex proceeds after the dehydration is complete. Such a tendency was also observed in *trans*-$[CrBr_2pn_2]Br\cdot H_2O$. In contrast to those chromium(III) complexes, the isomerization of the cobalt(III) complexes such as *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ is always accompanied by dehydration.4,5) This conspicuous difference in the thermal reaction might arise from the difference in mechanism of the isomerization.

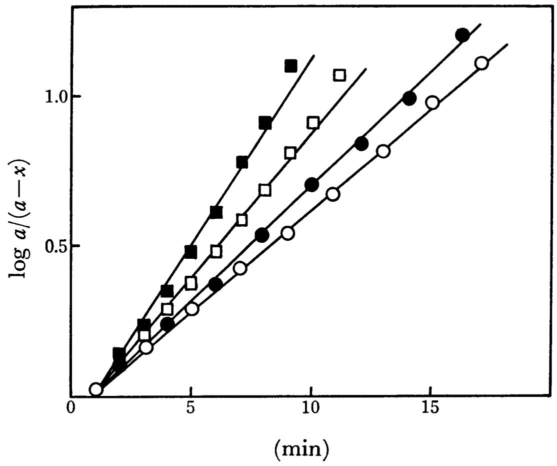


Fig. 3. Relation of log $a/(a-x)$ *vs.* time for the dehydration.

○129°C, ●136°C, □144°C, ■155°C.

The enthalpy change, ΔH, of the dehydration was obtained by analysis of the endothermic curve in the derivatogram to be 25 kJ mol^{-1}. The value is twice to that for *trans*-$[CrBr_2pn_2]Br\cdot H_2O$, 12.6 kJ mol^{-1}.

Rate of Dehydration. If the rate of dehydration at each temperature follows the first order law, the following equation holds:

$$2.303 \log \frac{a}{(a-x)} = k_d t,$$

where a and x are the initial amount of the starting complex and the amount of an anhydrous complex formed during time t, respectively, and k_d is the rate constant of dehydration. Approximately linear relationships were obtained (Fig. 3) when the values of log-$a/(a-x)$ were plotted *versus* t for each temperature. The rate constants at each temperature were obtained from the slopes of the respective lines. Their values are given in Table 1, together with those of isomerization (*vide post*). From the Arrhenius plots the activation energy of dehydration, E_d, was found to be 42 kJ mol^{-1}. This value is almost equal to the heat of evaporation of water. It is presumed, therefore, that the lattice water molecule in *cis*-$[CrCl_2tn_2]Cl\cdot0.5H_2O$ is bound loosely like liquid water.

Rate of Isomerization. If the rate of isomerization obeys the first order law, it could be expressed by the equation,

$$2.303 \log b/(b-y) = k_i t,$$

where b is the initial amount of the starting complex, *cis*-$[CrCl_2tn_2]Cl\cdot0.5H_2O$, y is the amount of *trans* complex produced during time t and k_i is the rate constant of isomerization.

TABLE 1. RATE CONSTANTS OF DEHYDRATION AND ISOMERIZATION

t °C	129	136	144	155	160	170	181	190	199	209
$k_d \times 10^{-3}$ s^{-1}	2.46	2.79	3.69	4.98						
$k_i \times 10^{-5}$ s^{-1}					1.40	3.56	10.44	22.52	59.11	126.0

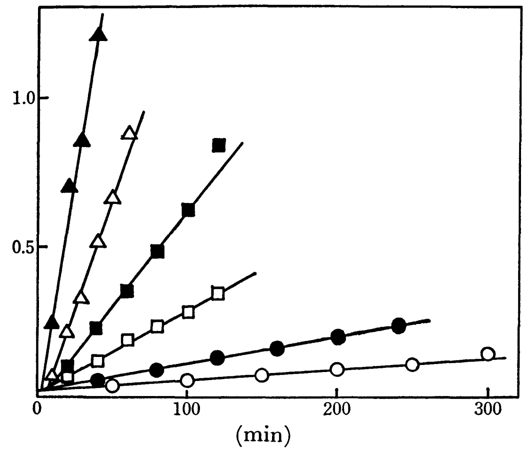


Fig. 4. Relation of log $b/(b-y)$ *vs.* time for the isomerization.
○ 160°C, ● 170°C, □ 181°C, ■ 190°C, △ 199°C, ▲ 209°C.

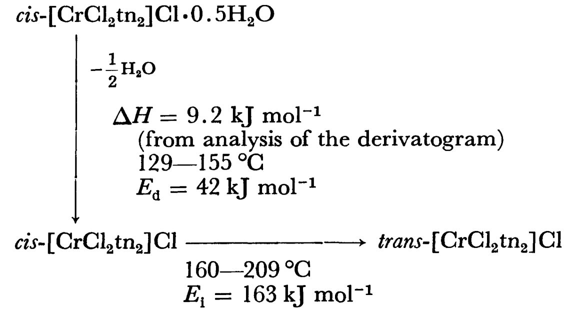
When the values of log $b/(b-y)$ were plotted **versus** *t* at each temperature, approximately linear relationships were also obtained (Fig. 4). The rate constants obtained from the slope of the respective lines are given in Table 1, together with those for dehydration. We see that the dehydration occurs at a relatively lower temperature, while most part of the isomerization proceeds in the higher temperature region.

From the Arrhenius plots of the rate constants, the activation energy, E_i, for the isomerization was calculated to be 163 kJ mol^{-1}. This value is slightly lower than 179.7 kJ mol^{-1} for the isomerization of *trans*-$[CrBr_2pn_2]Br\cdot H_2O$, but fairly greater than 96.1 kJ$\cdot mol^{-1}$ for that of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and 117.0 kJ mol^{-1} for that of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$.

As far as these complexes are concerned, the chromium(III) complexes give higher values of activation energy than the corresponding cobalt(III) complexes. This seems to be due to the fact that cobalt(III) complexes easily undergo isomerization with the aid of the lattice water through aqration-anation mechanism, whereas the chromium(III) complexes require excess energy for the structural change owing to the intramolecular rearrangement such as twisting or bond rupture in order to isomerize in anhydrous state. It should be noted that the coexistence of the lattice water noticeably causes the difference in the modes of isomerization between cobalt(III) and chromium(III) complexes.

It was found that the *trans*-to-*cis* isomerization occurs in the complexes $[MX_2pn_2]X\cdot HX\cdot nH_2O$ (M=Co or Cr; X=Cl or Br), where diamine forms a five-membered chelate ring, whereas the *cis*-to-*trans* isomerization takes place in the complex $[CrCl_2tn_2]Cl\cdot0.5H_2O$, in which the diamine forms a six-membered chelate ring, as also observed in the complexes $[CoCl_2tn_2]X\cdot H_2O$ (X=Cl, ClO_4) and $[CoBr_2tn_2]X\cdot H_2O$ (X=Br, ClO_4).

Thermochemical Reaction Scheme. The thermochemical reaction scheme for the path-way of the *cis*-to-*trans* isomerization of $[CrCl_2tn_2]Cl\cdot0.5H_2O$ can be expressed as follows.



The scheme for the dehydration and isomerization of *cis*-$[CrCl_2tn_2]Cl\cdot0.5H_2O$ is similar, except for the direction of isomerization, to that for *trans*-$[CrBr_2pn_2]Br\cdot H_2O$ in that isomerization occurs in an anhydrous state, but is quite different from that of the cobalt(III) complexes, *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$, in which isomerization takes place simultaneously with dehydration.

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