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Derivatographic Studies on Transition Metal Complexes. V.[1] Thermal *cis, trans*-to-*trans, cis* Isomerization of $[CoCl_2(NH_3)_2en]ClO_4$ in Solid Phase[2]

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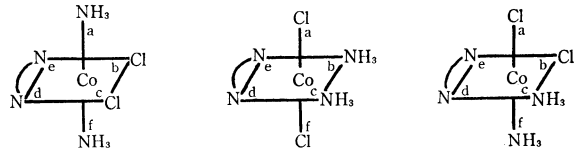
The complex, *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4$, regardless whether its state is monohydrate or anhydride, was isomerized to *trans,cis*-form by heating in a solid phase. In the kinetic study on perchlorate in a closed system, it was found that the isomerization of the hydrated compound proceeded through a second order reaction with respect to the remaining fraction of the starting compound with the activation energy, $E^{\neq}=29.5$ kcal mol^{-1}, while that of the anhydrous one proceeded through a first order reaction with $E^{\neq}=51.4$ kcal mol^{-1}. On the other hand, derivatographic analyses showed that the enthalpy change in the dehydration partly including isomerization was $\Delta H=13.9$ kcal mol^{-1} for the monohydrated perchlorate and the activation energy was $E^{\neq}=39.9$ kcal mol^{-1}, whereas the enthalpy change of isomerization of the anhydrous perchlorate was $\Delta H=-2.1$ kcal mol^{-1}. From the results, it is believed that the "Aquation-anation" mechanism on the crystal surface is predominant in the isomerization for the hydrate, but it proceeds through some intramolecular reactions for the anhydride.

The isomerization which takes place after complete dehydration has only recently been detected and reported for *trans*-$[CoCl_2(NH_3)_4]IO_3 \cdot 2H_2O$.[4,5] Typical examples as the above, where two steps of dehydration and *trans*-to-*cis* isomerization are obviously separated in a solid phase are relatively less in the field of thermochemistry of transition metal complexes. The thermal isomerization of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ to the corresponding *cis*-isomer[6,7] simultaneously gives rise to the loss of one molecule of hydrogen chloride and two molecules of crystalline water. The ammine complex, *trans*-$[CoCl_2(NH_3)_4]Cl$, undergoes partial isomerization accompanied by much decomposition at somewhat higher temperature.[5] In the case of the ethylenediamine complex, *trans*-$[CoCl_2en_2](H_5O_2)Cl_2$,[6] the corresponding isomerization was not detected.

Examples of *cis*-to-*trans* isomerization are much more rare.[8] It is expected in the complexes, *cis,trans*-$[CoCl_2(NH_3)_2en]X$, that, when the two adjacent chloride ions change their coordination sites to the *trans*-position upon heating, the color changes from blue to green.

Three geometrical isomers can be postulated for the above complexes as shown in Fig. 1. Distinct thermochromism from blue to green in a solid phase was observed in our preliminary experiments on the complex *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4$. A similar phenomenon was also observed for the anhydrous perchlorate. This is considered to correspond to the transformation from *cis,trans*- (a) to *trans,cis*- form (b) as shown in Fig. 1. The present study deals with the thermal isomerization of *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ and its anhydride to *trans,cis*-form complex.



(a) (b) (c)

Fig. 1. Three geometrical isomers of $[CoCl_2(NH_3)_2en]X$.
(a) *cis*(dichloro), *trans*(diammine)-form (*cis, trans*-form)
(b) *trans*(dichloro), *cis*(diammine)-form (*trans, cis*-form)
(c) *cis*(dichloro), *cis*(diammine)-form (*cis,cis*-form)

Experimental

Syntheses of Complexes. The complexes *trans,cis*- and *cis,trans*-$[CoCl_2(NH_3)_2en]Cl \cdot nH_2O$ were prepared by the known method.[9] The corresponding perchlorate were obtained from the respective chlorides by saturating their solutions with 60% perchloric acid at room temperature and by putting them to stand in a refrigerator for a while. The blue crystals corresponding to *cis,trans*-form complexes or the green crystals corresponding to *trans,cis*-form complexes deposited out were filtered and washed with a small amount of ethanol-water (2 : 1) and then ethanol-ether (1 : 1) mixtures, and dried over silica-gel in a desiccator for a while.

Found: C, 7.07; H, 4.70; N, 16.51%. Calcd for *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$: C, 7.03; H, 4.72; N, 16.41%.

Found: C, 7.52; H, 4.40; N, 17.25%. Calcd for *trans,cis*-$[CoCl_2(NH_3)_2en]ClO_4$: C, 7.43; H, 4.36; N, 17.32%.

The corresponding anhydrous *cis,trans*-compound was prepared by standing the monohydrate obtained above over silica-gel in a vacuum desiccator at room temperature for 10 days. The content of the crystalline water in the hydrate was sometimes determined with a thermobalance. In general, complete dehydration of the compound was achieved in a week at room temperature under similar conditions. Complete dehydration was also achieved even at 90°C in a few hours without any detectable isomerization. This was verified by the UV and IR spectral measurements.

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[1] For part IV in this series: see R. Tsuchiya, A. Uehara, and E. Kyuno, This Bulletin, **44**, 701 (1971).

[2] Presented at the 19th Symposium on Coordination Chemistry, Sendai, September, 1969.

[3] Present address: Showa Petroleum Industries, Co. Ltd., Yokohama.

[4] N. I. Lobanov, *Zh. Neorg. Khim.*, **4**, 344 (1959).

[5] H. E. LeMay, Jr., and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 5577 (1967).

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[7] R. Tsuchiya, K. Murai, A. Uehara, and E. Kyuno, This Bulletin, **43**, 1383 (1970).

[8] J. P. Mathieu and H. Poulet, *J. Chem. Phys.*, **59**, 369 (1962).

[9] J. C. Bailar, Jr., and D. F. Pepard, *J. Amer. Chem. Soc.*, **62**, 105 (1940).

Found: C, 7.62; H, 4.40; N, 17.25%. Calcd for $[CoCl_2(NH_3)_2en]ClO_4$: C, 7.43; H, 4.36; N, 17.32%.

Derivatographic Measurement. The derivatograms of these compounds were obtained with a MOM Derivatograph Typ-OD-102.[10] Samples in each run were 0.4 g, finely powdered, 100—200 mesh $inch^{-1}$. The measurements were carried out under a constant flow of nitrogen stream with the heating rate of 1°C min^{-1} unless otherwise stated. The enthalpy changes, ΔH, and the activation energies, $E^{\neq}$, in the thermal changes concerned were calculated by DTA curve analysis in the derivatograms.[11-13]

Spectral Measurements. Visible and UV absorption spectra of the complexes in solution were measured with a Hitachi R-3 Spectrophotometer. The IR spectral measurements of the complexes were carried out with a JASCO Model IR-E and IR-G Spectrophotometers in a Nujol mull.

Isothermal Measurements. The isothermal rate determination on dehydration was carried out with a Shimadzu TM-1A Thermobalance as a complement to derivatographic determinations. Measurements were carried out at several desired constant temperatures in a static air with the same samples as those used in the derivatographic study.

The rate of isomerization of the complexes was measured by using an Abderhalden apparatus keeping a small sample vessel under constant temperatures in a closed system. The products were taken out from the sample vessel at certain time intervals and the absorption spectra were measured to determine the mole ratio of *cis,trans*/*trans,cis* in the products.

The complex species, *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ and the corresponding *trans,cis*-form anhydride, are fairly soluble in dimethylformamide (DMF) in the original stable form, and the solution is found not to undergo further chemical change at least during the measurement. The absorption obeys Lambert-Beer's law within the concentration range for the determination. The pure complexes as shown in the spectra in Fig. 2, have the following absorption coefficients at 594 and 625 nm in DMF solution:

	ε_{594nm}	ε_{625nm}
cis,trans-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ and its anhydride	128.8	118.8
trans,cis-$[CoCl_2(NH_3)_2en]ClO_4$	33.8	43.8

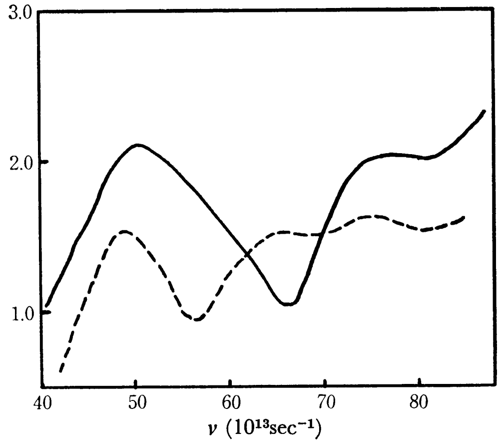

Fig. 2. Electronic spectra of $[CoCl_2(NH_3)_2en]ClO_4$ in DMF. ——, *cis,trans*-isomer; ----, *trans, cis*-isomer

From the results, the mixed mole ratio of two isomers in each product can be calculated spectrophotometrically by means of the equations

$$33.8X + 128.8Y = D_{594}$$
$$43.8X + 118.8Y = D_{625},$$

where X and Y are the concentrations in mol l^{-1} of *trans, cis*-complex and that of *cis,trans*-complex, respectively, and D_{594} and D_{625} the observed absorbancies at 594 nm and at 625 nm, respectively, with a 1.0 cm cell.

Results and Discussion

Dehydration of *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ proceeds through one step in TG and DTG curves, but the DTA gives a complicated pattern in the derivatogram as shown in Fig. 3. It is likely that the DTA curve in the derivatogram contains the overlapped heats of the two reactions, dehydration and isomerization. The DTA curve on the corresponding anhydrous complex, however, shows a small exothermic peak at about 160°C, probably due to isomerization, without any detectable mass loss as shown in Fig. 4.

The enthalpy change of the dehydration, including a partial isomerization, and that of the pure isomerization were derivatographically found to be $\Delta H = 13.9$ kcal mol^{-1} and -2.1 kcal mol^{-1}, from Fig. 3 and Fig. 4, respectively. Thus, the heat of pure dehydration for the perchlorate is presumed to be about 16 kcal mol^{-1}.

Dehydration containing a partial isomerization of *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ is considered to proceed through first order reaction, and the Arrhenius plots obtained on the basis of the above presumption are given in Fig. 5, from which the activation energy is calculated to be 36.6 kcal mol^{-1}.

When the complex, *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$, was heated in static air by a thermobalance under

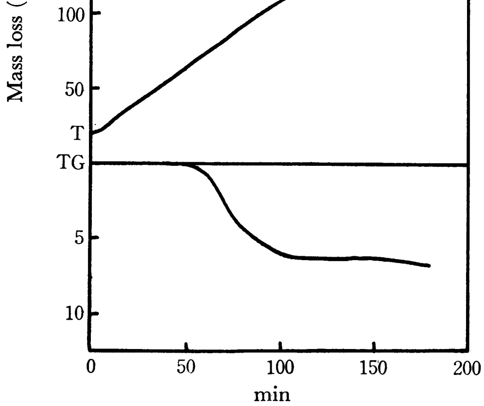

Fig. 3. Derivatogram for *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$.

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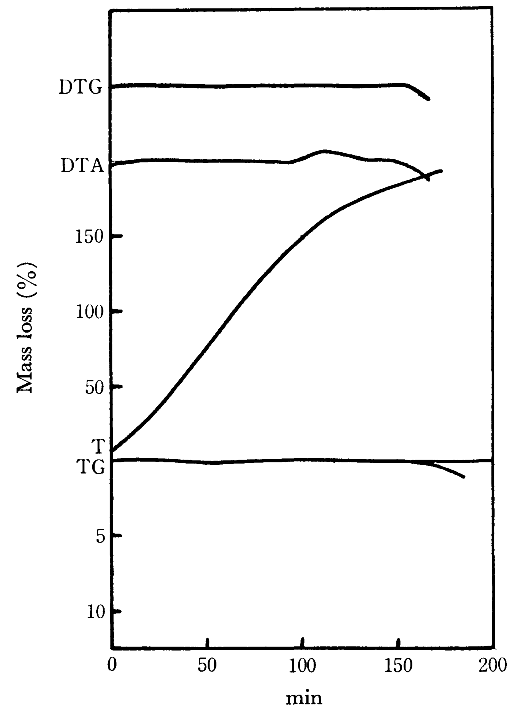


Fig. 4. Derivatogram for *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4$.

the heating rate of 0.5°C min^{-1}, dehydration began at 85°C, and isomerization started at 120°C after complete dehydration. When it was heated at 150°C, the product consisted of about 40% of the *trans,cis*-isomer and the remaining *cis,trans*-isomer. Isomerization was finally completed at 175°C. The IR spectrum for the product obtained at 175°C is shown in Fig. 6, together with those for monohydrated *cis,trans*-isomer and for anhydrous *trans,cis*-isomer directly prepared. The figure verifies that the final heating product is *trans,cis*-$[CoCl_2(NH_3)_2en]ClO_4$. A similar type isomerization was observed in the corresponding anhydrous perchlorate complex.

The rate constants of isomerization for the hydrated and anhydrous *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4$ in the closed system as well as those of dehydration in the static air were determined in an isothermal condition. The kinetic data are summarized in Table 1.

It is of interest that, in the closed system, isomerization for the hydrated complex was found to proceed in a second order reaction with respect to the remaining complex, and that for the anhydrous complex in first order. The presence of crystalline water might play some important role in the difference described above, but a reasonable explanation could not be obtained.

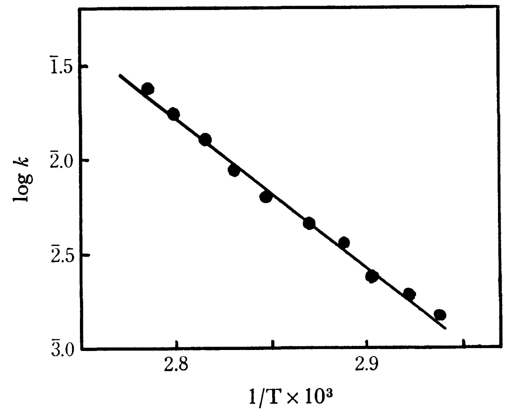


Fig. 5. Arrhenius plots for dehydration containing partial isomerization (derivatography).

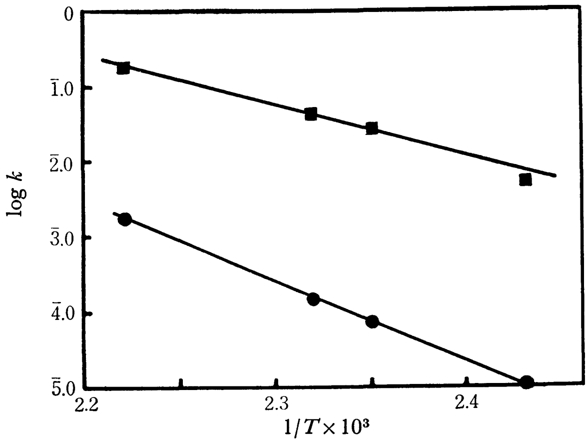


Fig. 7. Arrhenius plots for isomerization (isothermal measurement). -■-■-, *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$; -●-●-, *cis, trans*-$[CoCl_2(NH_3)_2en]ClO_4$

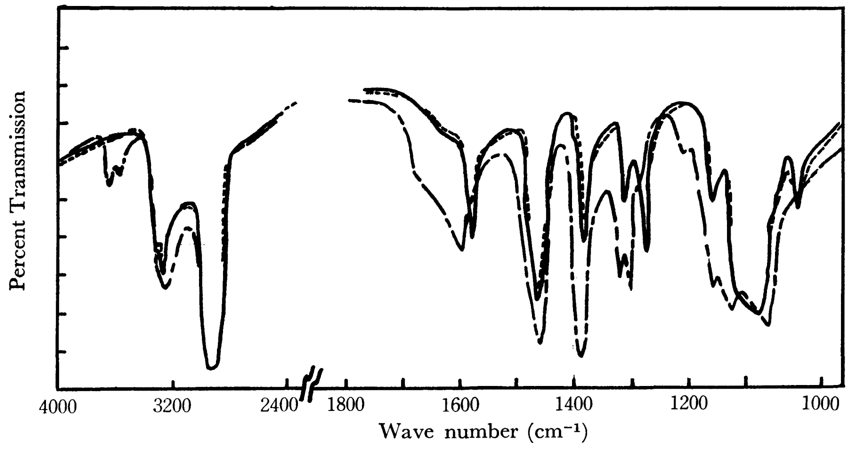
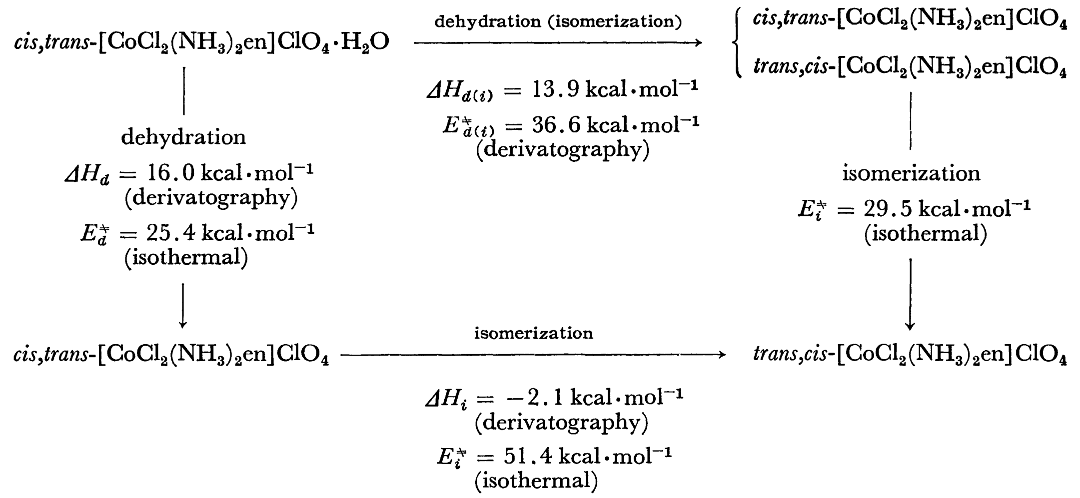


Fig. 6. IR spectra of the complexes. —·—, *cis, trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$; ······, *cis, trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ after heating at 175 °C; ——, *trans, cis*-$[CoCl_2(NH_3)_2en]ClO_4$.

Table 1. rate constants for *cis, trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ and its anhydride

	$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$				$[CoCl_2(NH_3)_2en]ClO_4$	
°C	K_d, sec^{-1}	$E_d^{\neq}$, kcal mol^{-1}	K_i, sec^{-1}	$E_i^{\neq}$, kcal mol^{-1}	K_i, sec^{-1}	E_i, kcal mol^{-1}
70	$(7.9\pm0.3)\times10^{-4}$					
80	$(2.8\pm0.2)\times10^{-3}$					
90	$(5.0\pm0.2)\times10^{-3}$	25.4				
100	$(1.2\pm0.2)\times10^{-2}$					
138			$(2.0+0.2)\times10^{-3}$		$(7.5\pm0.2)\times10^{-6}$	
153			$(2.8\pm0.2)\times10^{-2}$		$(5.2\pm0.2)\times10^{-5}$	
158			$(4.1\pm0.2)\times10^{-2}$	29.5	$(1.2\pm0.2)\times10^{-4}$	51.4
178			$(2.0\pm0.2)\times10^{-1}$		$(1.2\pm0.2)\times10^{-3}$	

k_d and k_i are the rate constants of isomerization and those of dehydration.
$E_d^{\neq}$ and $E_i^{\neq}$ are the corresponding activation energies.



ΔH_d, ΔH_i and $\Delta H_{d(i)}$ represent to enthalphy changes of dehydration, isomerization, and dehydration containing partial isomerization.

$E^{\neq}_{d(i)}$ denotes the activation energy of dehydration containing partial isomerization.

Fig. 8. Schematic diagram for thermal reactions on *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$.

The Arrhenius plots concerned are shown in Fig. 7, from which the activation energies for isomerization were calculated to be 29.5 kcal mol^{-1} and 51.4 kcal mol^{-1} for the monohydrate and anhydride, respectively.

The thermal reaction pathways concerning *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ and the thermal functions corresponding to the respective steps obtained are summarized schematically in Fig. 8.

The value of activation energy for the isomerization of *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4 \cdot H_2O$ was found to be of a similar order to that of the *trans*-to-*cis* isomerization of $[CoCl_2pn_2](H_5O_2)Cl_2$ under similar conditions.[7] Thus, the mechanism for the isomerization of the former hydrated complex seems to be explained by that of "aquation-anation" in closed system, as presumed in the latter complex.

Since remarkably higher activation energy is necessitated for the reaction in first order, isomerization of the anhydrous complex suggests an intramolecular reaction mechanism, *e. g.*, "twist" or "chelate ring opening-closing," because a similar mechanism has been also postulated for the isomerization of *trans*-to-*cis* reaction of $[CoCl_2pn_2]Cl$.[7] The difference between the activation energy from the derivatograms and that from the results obtained in a closed system may be due to the fact that the former contains both the data of isomerization and a part of dehydration and the latter that of isomerization only.