March, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 709—712 (1971)

Derivatographic Studies on Transition Metal Complexes. VI.[1] Thermal, *cis*, *trans*-to-*cis*, *cis* Exchange-Isomerization[2] of $[CoCl_2(NH_3)_2en]SCN\cdot H_2O$ in Solid Phase[3]

Ryokichi Tsuchiya, Masatatsu Suzuki, and Eishin Kyuno
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

(Received August 27, 1970)

The exchange-isomerization of the complex, *cis*(dichloro), *trans*(diammine)-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$ to *cis*-(chloro isothiocyanato), *cis*(diammine)-$[CoCl(NCS)(NH_3)_2en]Cl$, was investigated by means of both derivatographic and isothermal methods. The reaction took place immediately after the liberation of crystalline water. The thermochemical functions were obtained to be $\Delta H=(5.5\pm1.0)$ kcal/mol and $E^{\neq}=(22.8\pm2.0)$ kcal/mol for the dehydration, while those for the exchange-isomerization were $\Delta H=(4.8\pm1.0)$ kcal/mol and $E^{\neq}=(62.3\pm3.0)$ kcal/mol, respectively. As a probable reaction mechanism for the exchange-isomerization, a certain seven coordinated intermediate in the reaction pathway was introduced.

Recently, several examples of thermal, *cis*-to-*trans*[1,4] and *trans*-to-*cis*[5–7] isomerization on transition metal complexes in solid phase have been reported. The different mechanisms were proposed between the thermal isomerization including dehydration in the hydrated solid phase and that in anhydrous phase; *i. e.*, "aquation-anation" mechanism was well fitted for the former isomerization and "twisting"[8] or "chelate ring opening-closing" mechanism[9] were mainly applied to the latter.

Although the exchange-isomerization in solid phase on transition metal complexes containing the simultaneous occurrence of the isomerization and exchange reaction between the ligand coordinated and the counter ion in the outer sphere is very rare, it is known that a similar reaction sometimes takes place in the case of using matrix-method[10] for the preparation of the complexes.

When the compound, *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$, was heated in solid phase, the following reactions occurred successively:

$$\textit{cis,trans}\text{-}[CoCl_2(NH_3)_2en]SCN\cdot H_2O \longrightarrow \textit{cis,trans}\text{-}[CoCl_2(NH_3)_2en]SCN + H_2O \quad \text{(Dehydration)} \qquad (1)$$

$$\textit{cis,trans}\text{-}[CoCl_2(NH_3)_2en]SCN \longrightarrow \textit{cis,cis}\text{-}[CoCl(NCS)(NH_3)_2en]Cl \quad \text{(Exchange-isomerization)} \qquad (2)$$

The distinct color change, from blue to violet, was found in the reaction (2) at the temperature near 135°C. The present paper is concerned with the dehydration (1) and the exchange-isomerization (2) described above.

Experimental

Preparation of the Complex. The complex, *cis,trans*-$[CoCl_2(NH_3)_2en]Cl$, was prepared by the known method.[11] The corresponding thiocyanate was obtained by saturating the solution of the pure chloride with potassium thiocyanate. The row product was recrystallized in a dilute potassium thiocyanate solution. The blue crystals collected by filtration were washed with small amounts of cold water, ethanol and ether in turn and air-dried.

Found: C, 12.01; H, 5.17; N, 22.97%. Calcd for *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$: C, 12.00; H, 5.38; N, 23.48%.

Derivatographic Measurement. The apparatus and techniques used in this work were the same as described in an earlier paper.[6]

Isothermal Measurement by using a Thermobalance. The measurement and analytical method for the experiments were also the same in an earlier paper.[12] Determination of the mixed ratio of two compounds, the starting *cis,trans*-form complex and *cis,cis*-form produced, was made spectrophotometrically.

Results and Discussion

Structural Determination of Reaction Product from the Spectra. The complex, $[CoClX(NH_3)_2en]^+$ is expected to exist in either of the four geometrical isomers as given in Fig. 1.

The infrared absorption spectra of $[CoCl(NCS)(NH_3)_2en]Cl$ produced and of the related compounds the structure of which is clear are shown in Fig. 2. It has been well known that, in general, the cobalt(III) complexes which have the two ammine groups in *cis*-

---

1) Part V in this series: see R. Tsuchiya, A. Nakata, and E. Kyuno, This Bulletin, **44**, 705 (1971).

2) This was termed for the reaction consisting of both isomerization and ligand-exchange at the same time.

3) Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

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

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

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

7) Y. Kaji, A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 1906 (1970).

8) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958); P. C. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **18**, 289 (1941); *ibid.*, **20**, 81 (1943).

9) See, for example, F. Basolo, and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd Ed., John Wiley & Sons, Inc., New York (1967) p. 327.

10) W. W. Wendlandt and L. K. Sveum, *J. Inorg. Nucl. Chem.*, **28**, 393 (1966).

11) J. C. Bailar, Jr., and F. Pepard, *J. Amer. Chem. Soc.*, **62**, 105 (1940).

12) R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, This Bulletin, **42**, 1881 (1969).

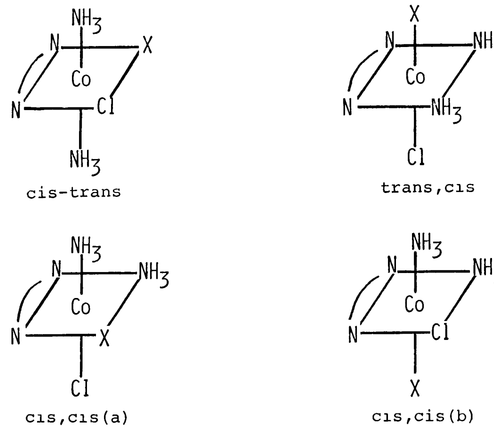

Fig. 1. Four geometrical isomers of $[CoClX(NH_3)_2en]^+$ (X= Cl^- or NCS^-).

position give two peaks assigned to the symmetric deformation, δ_{NH_2}, in the region of 1400—1200 cm^{-1} in the IR spectra, while *trans*-diammine ones have only one peak in this region: *e. g.*, the *cis*-diammine complexes involving organic amine like the ethylenediamine or propylenediamine, *trans,cis*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$[13,14] and *trans,cis*-$[CoCl_2(NH_3)_2pn]Cl\cdot H_2O$,[15] show two peaks at 1310 and 1280 cm^{-1}, respectively, while the *trans*-diammine complexes, *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$, *cis,trans*-$[CoCl_2(NH_3)_2pn]Cl\cdot H_2O$[16] and *cis,trans*-$NH_4[Co(SO_3)_2(NH_3)_2en]\cdot 2H_2O$,[11] have also two neighboring peaks at 1310 and 1330 cm^{-1} in rather higher wave number region than that given by the *cis*-diammine complexes. It has been understood by the fact that the bands assigned to the symmetric deformation, δ_{NH_2}, of ammonia and of organic amine are overlapped in this region.

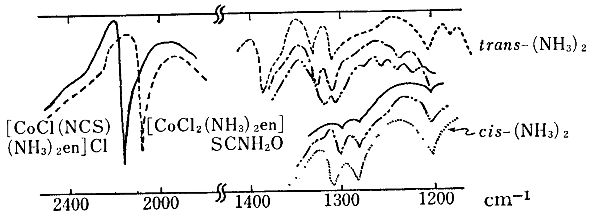

Fig. 2. IR spectra for the complexes.
cis, trans-$[CoCl_2(NH_3)_2en]$ $SCN\cdot H_2O$ (------)
cis, trans-$[CoCl_2(NH_3)_2pn]Cl\cdot H_2O$ (-··-··-)
cis, trans-$NH_4[Co(SO_3)_2(NH_3)_2en]\cdot 3H_2O$ (-·-·-)
cis, cis-$[CoCl(NCS)(NH_3)_2en]Cl$ (——)
trans, cis-$[CoCl_2(NH_3)_2pn]Cl\cdot H_2O$ (-··-··-)
trans, cis-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$(·········)

When the complex *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$ was heated, the color changed from blue to violet and the two peaks at 1310 and 1330 cm^{-1} of the starting material were shifted to lower wave number side at 1280 and 1310 cm^{-1} in their IR spectra as shown in Fig. 2.

From the above results, it is clearly recognizable that the structural change, from *trans*-diammine to *cis*-diammine, may be involved in the thermal reaction. It has also been found that the band of the starting complex assigned to the stretching vibration, $\nu_{C=N'}$,[17,18] was shifted from 2080 cm^{-1} to 2160 cm^{-1} upon heating it. This shift should include the exchange between chloride coordinated to central metal ion and thiocyanate in counter-ion sphere.

In addition, an interesting information derived from the change in the frequency of the $\nu_{C=N}$ band comes whether or not the linkage isomerism by the coordination of -SCN or -NCS occurs in the exchange reaction. The evidence is not very much clear, but it seems that the ligand coordinates as -NCS toward the central metal atom in this case based on the analysis of IR spectrum.[18]

It has been well known that one of the most available method in determining the geometrical structure of the transition metal complexes is the use of the analysis of electronic spectra. Since a very large difference on the electronic spectra[19] between the complexes involving two negative ligands in the *cis* position and the corresponding ones in the *trans* position has been found clearly, it will be possible to decide whether *cis* or *trans* position is occupied by these ligands coordinated in the unknown geometrical structure. The electronic spectra of $[CoCl(NCS)(NH_3)_2en]Cl$ and of the related complexes are shown in Fig. 3.

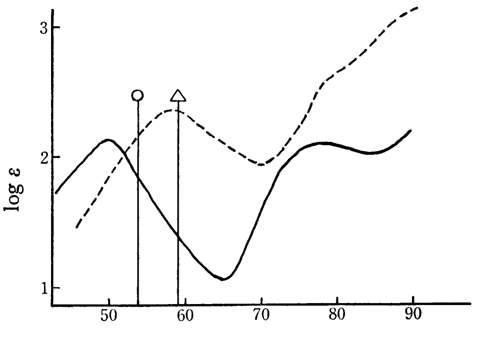

Fig. 3. Electronic spectra for *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$(——) and *cis,cis*-$[CoCl(NCS)(NH_3)_2en]Cl$ (······) (○ and △ indicate the frequencies of absorption maxima for *trans*-$[CoCl(NCS)en_2]Cl$ and *cis*-$[CoCl(NCS)en_2]Cl$, respectively.).

Aside from the appearance of the band splitting tendency[19] when such negative ligands are involved in the *cis* position as in the case of *cis,cis*-$[CoCl(NCS)(NH_3)_2en]Cl$[14] and *cis*-$[CoCl(NCS)en_2]Cl$,[20] the band exists in the rather higher frequency region than that of the corresponding *trans* one, *trans*-$[CoCl(NCS)en_2]Cl$.[14] The first absorption band of bis(ethylenedi-

---

[13] For *cis, trans*- and *trans, cis*-$[CoCl_2(NH_3)_2en]Cl$: E. Kyuno, *Nippon Kagaku Zasshi*, **80**, 722 (1959).

[14] M. E. Baldwin, *J. Chem. Soc.*, **1960**, 4369.

[15] To be published elsewhere.

[16] To be published elsewhere.

[17] J. C. Bailar, Jr., and M. M. Chamberlain, *J. Amer. Chem. Soc.*, **81**, 6412 (1959).

[18] P. O. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, **1960**, 1912.

[19] See for examples: K. Nakamoto, J. Fujita, M. Kobayashi, and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957) and H. Yamatera, This Bulletin, **31**, 95 (1956).

[20] H. Kuroya and R. Tsuchida, This Bulletin, **15**, 427 (1940).

amine) complexes, in general, appears in slightly higher frequency region than that of diammine-ethylenediamine one, being obeyed on "Spectrochemical Series".[21] The utility of the empirical rule in this case suggests that the product, [$CoCl(NCS)(NH_3)_2en$]Cl from *cis,trans*-[$CoCl_2(NH_3)_2en$]$SCN \cdot H_2O$ by the thermal reaction is still held the *cis* structure with respect to two negative ligands coordinated in spite of exchange of one of the ligands.

Kinetic Studies. The derivatogram for *cis,trans*-[$CoCl_2(NH_3)_2en$]$SCN \cdot H_2O$ is given in Fig. 4. When the complex was heated at the heating rate 1° min^{-1} by using Derivatograph, the loss of crystalline water began at about 75°. The TG curve indicates that the dehydration is completed up to 120° and no further mass loss was detected until about 170°. The DTA curve exhibits two endothermic peaks corresponding to dehydration and the genuine decomposition of the complex, respectively. And one more small exothermic peak appears at about 135° without the change of both TG and DTG curves in the derivatogram, where the color change from blue to violet was, however, found, which is corresponding to the exchange-isomerization, *cis,trans*-[$CoCl_2(NH_3)_2en$]$SCN \longrightarrow$ *cis,cis*-[$CoCl(NCS)$-$(NH_3)_2en$]Cl. From the situation, it is possible to conclude that the exchange-isomerization proceeds after the dehydration process.

The experimental thermochemical functions calculated from the derivatogram were $\Delta H = (5.5 \pm 1.0)$ kcal/mol and $E^{\neq} = (22.8 \pm 2.0)$ kcal/mol for the dehydration, and $\Delta H = (4.8 \pm 1.0)$ kcal/mol and $E^{\neq} = (62.3 \pm 3.0)$ kcal/mol for the exchange-isomerization, and the Arrhenius plots for the calculation of the activation energy are shown in Fig. 5.

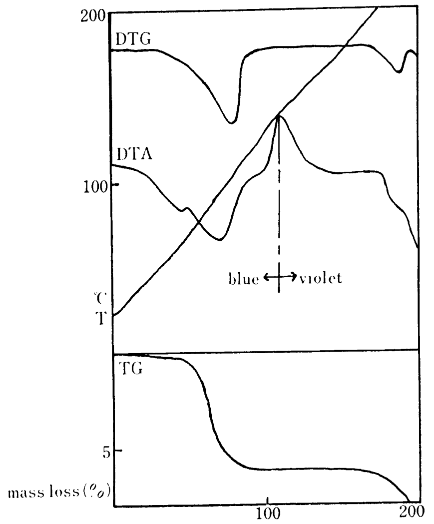

Fig. 4. Derivatogram for *cis,trans*-[$CoCl_2(NH_3)_2en$]$SCN \cdot H_2O$.

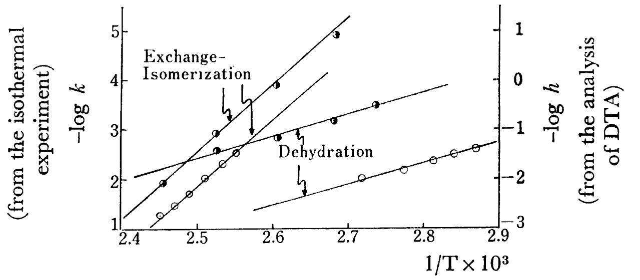

Fig. 5. The Arrhenius plots for *cis, trans*-[$CoCl_2(NH_3)_2en$]-$SCN \cdot H_2O$ from isothermal (◐) and from DTA analysis(○).

The thermal exchange-isomerization of *cis,trans*-[$CoCl_2(NH_3)_2en$]$SCN \cdot H_2O$ was also studied by means of isothermal method. At a certain constant temperature, the mole ratio of the *cis,trans*-form complex against the *cis,cis*-form complex produced was estimated every after several different times. Since pure *cis,trans*-[$CoCl_2$-$(NH_3)_2en$]$SCN \cdot H_2O$ and *cis,cis*-[$CoCl(NCS)(NH_3)_2en$]-Cl show the absorption coefficients, 168 and 58.3 at 518 nm, and 65.3 and 121.5 at 598 nm in DMF, respectively, the *cis,trans*/*cis,cis*-ratio in the product in each step can be determined spectrophotometrically by means of the following equations:

$$168X + 58.3Y = D_{518}$$
$$65.3X + 121.5Y = D_{598},$$

where X and Y are the concentrations (in mol l^{-1}) of *cis,trans*- and *cis,cis*-complexes, and D_{518} and D_{598} are the absorbancies at 518 and 598 nm with 1.0 cm cell, respectively. Thus, *cis,trans*/*cis,cis*-ratios are given by X/Y.

From the mole ratio obtained above, the rate constants of dehydration, k_d, and of exchange-isomerization, k_i, were calculated, which are summarized in Table 1.

TABLE 1. THE RATE CONSTANTS OF DEHYDRATION, k_d AND OF EXCHANGE-ISOMERIZATION, k_i, IN ISOTHERMAL MEASUREMENTS

Temp. (°C)	k_d (sec^{-1})	k_i (sec^{-1})
90	$(1.6 \pm 0.4) \times 10^{-4}$	
100	$(4.9 \pm 0.4) \times 10^{-4}$	$(8.5 \pm 0.3) \times 10^{-6}$
110.8	$(9.2 \pm 0.4) \times 10^{-4}$	$(7.1 \pm 0.3) \times 10^{-5}$
121.1	$(1.5 \pm 0.2) \times 10^{-3}$	$(6.7 \pm 0.3) \times 10^{-4}$
138.3		$(8.0 \pm 0.2) \times 10^{-3}$

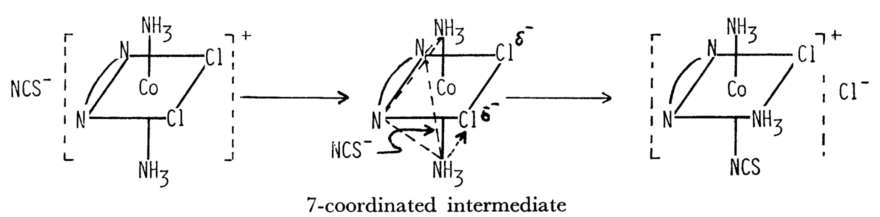

Fig. 6. The possible mechanism for exchange-isomerization of *cis, trans*-[$CoCl_2$-$(NH_3)_2en$]$SCN \cdot H_2O$ to *cis, cis*-[$CoCl(NCS)(NH_3)_2en$]Cl.

---

[21] Y. Shimura and R. Tsuchida, This Bulltein, **29**, 311 (1956).

The Arrhenius plots are given in Fig. 5, together with those obtained from derivatography. The thermochemical functions calculated from the isothermal measurement were $E^{*}=(20.1\pm2)$ kcal/mol and (62.3 ± 3.0) kcal/mol for the dehydration and exchange-isomerization, respectively, which are in good agreement with the corresponding data from the derivatography.

The possible reaction mechanism for the exchange-isomerization of *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$ to *cis,cis*-$[CoCl(NCS)(NH_3)_2en]Cl$ in the solid phase may be proposed as shown in Fig. 6. It is likely that a a certain intramolecular thermal reaction proceeds through seven coordinated intermediate by the action with SCN^- as the counter ion in the second coordination-sphere. The product by this mechanism should have *cis,cis*-b structure as shown in Fig. 1, if the incoming SCN^- group attacks the *trans* side to the negative coordinated chloride ligand, and as the result, one of Cl^- may be removed from the seven coordinated intermediate by push-effect of NCS ligand.

When the SCN ligand approaches to the central cobalt ion, the linkage: M–NCS will prefer to that of M–SCN. However, there is still no evidence whether the final product is *cis,cis*-a or -b.