Derivatographic Studies on Transition Metal Complexes. XI.[1] Thermal Ligand-exchange Reaction of *cis*- and *trans*-$[CoXY(N_4)]SCN \cdot nH_2O$ Type Complexes[2]

Ryokichi Tsuchiya, Tatsuo Murakami,* and Eishin Kyuno
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

(Received April 20, 1973)

The thermal ligand-exchange reaction was investigated by derivatographic and isothermal methods for the following complex thiocyanates: *cis*-$[CoCl_2en_2]SCN$, *cis*-$[CoClBren_2]SCN \cdot H_2O$, *cis*-$[CoBr_2en_2]SCN \cdot H_2O$ and the corresponding *trans*-complexes, and several corresponding triethylenetetramine complexes *cis*-α-[CoXYtrien]-$SCN \cdot H_2O$, where X and Y represent Cl^- and Br^- ion, respectively. *cis*-Complexes, except for *cis*-$[CoCl_2en_2]SCN$ were found to exhibit obviously the ligand-exchange reaction in which Cl^- or Br^- is substituted by SCN^- just after the liberation of lattice water takes place. On the other hand, *cis*-$[CoCl_2en_2]SCN$ showed only partial ligand-exchange reaction accompanied by immediate thermal decomposition even at higher temperature than in the other monohydrates. In contrast, all the anhydrated *trans*-complexes *trans*-$[CoCl_2en_2]SCN$, *trans*-$[CoClBren_2]$-SCN and *trans*-$[CoBr_2en_2]SCN$ did not give such a reaction upon heating. The activation energies of *cis*-$[CoClBren_2]SCN \cdot H_2O$ were found to be $E_a = 26 \pm 2$ kcal/mol for dehydration and $E_a = 54 \pm 2$ kcal/mol for ligand-exchange. The thermal ligand-exchange reaction proceeded in *cis*-type complexes without change in the geometrical configuration of the original complexes. No racemization or inversion could be observed in the optically active complex.

Of several types of thermal reactions on transition metal complexes in a solid phase, the isomerization reactions for *trans*-$[CoCl_2(NH_3)_4]IO_3 \cdot 2H_2O$,[3] *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4$[4] and *trans*-$[CoCl_2pn_2](H_5O_2) \cdot Cl_2$,[5,6] and the racemization reactions for *d*-*cis*-$[CrCl_2en_2]Cl$,[7] *d*-$[Coen_3]I_3 \cdot H_2O$,[7] and *l*-$K_3[Co(C_2O_4)_3] \cdot nH_2O$[8,9] have been reported. In most cases, solid phase reactions occurred without exchange of the ligand by counter ions. However, few studies have been carried out on the ligand-exchange reaction between anionic ligand coordinated and the counter ion in outer coordination sphere.

Radioactive chloride exchange reaction takes place when *trans*-$[Co^*Cl_2pn_2](H_5O_2) \cdot Cl_2$ or *trans*-$[CoCl_2pn_2](H_5O_2) \cdot {}^*Cl$ is heated.[6] In this reaction, the complete chloride scrambling might occur during the course of dehydration or dehydrochlorination. This suggests that the aquation-anation mechanism is acceptable.

Another type of thermal exchange reaction was found[10] in *cis,trans*-$[CoCl_2(NH_3)_2en]SCN \cdot H_2O$. It contains not only stereochemical change in the coordination sphere but also ligand-exchange with the counter ion: *i.e.*, the reaction of this complex proceeds in two steps as follows.

(1) *cis, trans*-$[CoCl_2(NH_3)_2en]SCN \cdot H_2O$
$\rightarrow$ *cis, trans*-$[CoCl_2(NH_3)_2en]SCN + H_2O$

(2) *cis, trans*-$[CoCl_2(NH_3)_2en]SCN$
$\rightarrow$ *cis, cis*-$[CoCl(NCS)(NH_3)_2en]Cl$

In (2) the stereochemical change and ligand-exchange occur simultaneously, water of crystallization playing no important role. For thermal reaction in this complex, an associative mechanism with seven coordinated reaction intermediates was proposed.[10]

Thermal reaction in a solid phase is affected by several factors, one of which is the steric effect of a chelate ring. Thus, it is of interest to investigate the effect of chelation of neutral ligands in *cis*- and *trans*-$[CoXY(N_4)]SCN \cdot nH_2O$, as compared with *cis,trans*-$[CoCl_2(NH_3)_2en]SCN \cdot H_2O$. Coordinated halogen ions will also affect the thermal reaction.

We have also attempted to survey the role of lattice water on the ligand-exchange reaction and examine the influence of isomeric configurations of starting complexes; *viz.*, the effect brought about by the difference in coordination site of two halogen ions.

We have prepared *cis*- and *trans*-$[CoXY(N_4)]SCN \cdot nH_2O$ type complexes and investigated their thermal ligand-exchange reactions in detail.

Experimental

Preparation of Complex Thiocyanates. Complexes *cis*-$[CoCl_2en_2]Cl$, *cis*-$[CoClBren_2]Br$ and *cis*-$[CoBr_2en_2]Br$ and the corresponding trans complexes were prepared by the methods in literature.[11,12] Their thiocyanates were obtained by adding an excess amount of potassium thiocyanate to the cold saturated solution of the corresponding chloride or bromide. Recrystallization was carried out from a dilute solution of potassium thiocyanate. The crystals were filtered and washed with small amounts of water, ethanol and ether

---

* Present address: Fuji Kagaku Kogyo Co., Ltd., Kami-ichi, Toyama.

[1] Part X of this series; R. Tsuchiya, S. Joba, A. Uehara, and E. Kyuno, This Bulletin, **46**, 1454 (1973).

[2] Presented in part at the 20th Annual Meeting of the Chemical Society of Japan, Hiratsuka, 4, April, 1972.

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

[4] R. Tsuchiya, A. Nakata, and E. Kyuno, This Bulletin, **44**, 705 (1971).

[5] R. Tsuchiya, K. Murai, and E. Kyuno, *ibid.*, **43**, 1383 (1970).

[6] H. E. LeMay, Jr., *Inorg. Chem.*, **10**, 1990 (1971).

[7] H. E. LeMay, Jr. and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **90**, 1729 (1968).

[8] J. Brady, F. Dachille, and C. D. Schmulbach, *Inorg. Chem.*, **2**, 803 (1963).

[9] J. Brady, F. Dachille, and C. D. Schmulbach, *ibid.*, **7**, 287 (1968).

[10] R. Tsuchiya, M. Suzuki, and E. Kyuno, This Bulletin, **44**, 709 (1971).

[11] W. C. Fernelius, "Inorganic Synthesis," Vol. 2, p. 223 (1946); *ibid.*, Vol. 9, p. 163 (1967).

[12] A. Werner, L. J. Lorie, and J. Rapiport. *Ann*, **386**, 112 (1912).

Table 1. Elemental analysis

Complex	C%		H%		N%	
	Found	Calcd	Found	Calcd	Found	Calcd
trans-[CoCl$_2$en$_2$]SCN	19.60	19.49	5.74	5.24	22.07	22.73
trans-[CoClBren$_2$]SCN	17.32	17.03	4.77	4.58	19.87	19.87
trans-[CoBr$_2$en$_2$]SCN	15.42	15.12	4.34	4.07	17.40	17.64
cis-[CoCl$_2$en$_2$]SCN	19.56	19.49	5.53	5.24	22.42	22.73
cis-[CoClBren$_2$]SCN·H$_2$O	16.78	16.20	4.66	4.91	18.77	18.90
cis-[CoBr$_2$en$_2$]SCN·H$_2$O	15.04	14.47	4.52	4.38	17.07	16.88
cis-α-[CoCl$_2$trien]SCN·H$_2$O	23.92	23.87	5.89	5.74	19.83	19.89
cis-α-[CoClBrtrien]SCN·H$_2$O	21.28	21.19	5.25	5.01	17.90	17.66
cis-α-[CoBr$_2$trien]SCN·H$_2$O	19.31	19.06	4.77	4.58	16.33	15.88
(−)$_D$-*cis*-α-[CoBr$_2$trien]SCN·H$_2$O	19.36	19.06	4.70	4.58	16.36	15.88

and then air-dried.

The triethylenetetramine complexes *cis*-α-[CoCl$_2$trien]Cl,[13] *cis*-α-[CoClBrtrien]Br[14] and *cis*-α-[CoBr$_2$trien]Br[15] were obtained by the known methods. The thiocyanates were obtained by a similar method to that for the corresponding ethylenediamine complexes. The optically active complex (−)$_D$-*cis*-[CoBr$_2$trien]SCN·H$_2$O was obtained by the reaction of (−)$_D$-*cis*-α-[CoBr$_2$trien]Br with potassium thiocyanate in an aqueous solution.

The complexes obtained were identified by elemental analysis and spectral measurement. The results are given in Table 1.

Derivatographic Measurement. The apparatus and technique for derivatography were the same as described previously.[5]

Isothermal Measurement. A Shimadzu TM-1A Thermanobalance and an Abderhalden apparatus were used for isothermal measurement. The procedures of measurement and analysis were also the same as given previously.[16]

Spectral Measurement. The electronic, infrared and circular dichroism spectra were measured with a Hitachi ERS spectrophotometer, JASCO Model IR-E, IR-F spectrophotometer, and JASCO Model ORD/UV-5 spectrophotometer, respectively.

Results and Discussion

Structure of Reaction Products. When freshly prepared *cis*-type complexes except for *cis*-[CoCl$_2$en$_2$]-SCN were heated, the original violet color turned brick-red, showing that the counter ion may coordinate in place of halogen ligand after dehydration. The IR spectra of *cis*-[CoClBren$_2$]SCN·H$_2$O and the reaction product are shown in Fig. 1.

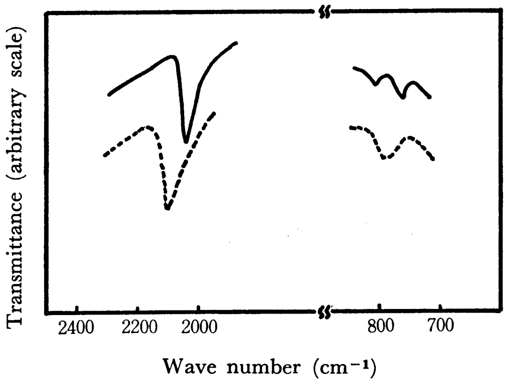

Fig. 1. IR spectra of *cis*-[CoClBren$_2$]SCN·H$_2$O (——) and its reaction product (----).

We see that C≡N stretching band is shifted from 2040 cm^{-1} to 2100 cm^{-1} upon heating. It is well-known[17] that there is a characteristic difference between the infrared spectra of the complexes containing SCN$^-$ of different coordination modes and those of the complexes having SCN$^-$ as counter ion, *viz.*, the infrared absorption band assigned to C≡N stretching vibration in the thiocyanate ion attached to a metal ion appears in the higher wavenumber region than that in the inorganic thiocyanate anion. The shift from 2040 cm^{-1} to 2100 cm^{-1} may be attributed to a cobalt(III)-thiocyanate bonding formation, and the thiocyanate ion in outer sphere probably coordinates to the central metal after dehydration.

The linkage isomerism of N-bonded or S-bonded thiocyanate ion in the coordination is distinct from the presence of a C–S stretching vibration band in the frequency region 690—860 cm^{-1} and NCS bending in the region 400—490 cm^{-1}. It is known[17] that the C–S stretching band appears in 780—860 cm^{-1} for M–NCS and 690—720 cm^{-1} for M–SCN and NCS bending band, in 450—490 cm^{-1} for M–NCS and 400—440 cm^{-1} for M–SCN.

After the exchange reaction is over, the C–S stretching band shifts towards the higher wave number region from 760 cm^{-1} which is given by SCN$^-$ counter ion, partly overlapping the NH$_2$ deformation band. Although there is no obvious evidence for the change of frequency in NCS bending, it may be concluded that the thiocyanate ion participates in bonding through nitrogen atom to central cobalt(III) ion.

The IR spectra of *cis*-[CoBr$_2$en$_2$]SCN·H$_2$O and its reaction product are very similar to those of *cis*-[CoClBren$_2$]SCN·H$_2$O.

---

[13] E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **87**, 4458 (1965).

[14] E. Kyuno, and J. C. Bailar, Jr., *ibid.*, in press.

[15] E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1125 (1966).

[16] R. Tsuchiya, Y. Kaji, and E. Kyuno, This Bulletin, **42**, 1881 (1969).

[17] P. C. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, **1960**, 1912; K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd Ed., John Wiley & Sons, Inc., New York (1970), p. 187.

Table 2. Absorption maxima of starting complexes and reaction products

	Starting complex	Reaction product
cis-$[CoCl_2en_2]SCN$	540 (2.11)	a)
cis-$[CoClBren_2]SCN\cdot H_2O$	549 (2.03)	505 (2.21)
cis-$[CoBr_2en_2]SCN\cdot H_2O$	554 (2.05)	510 (2.25)
cis-α-$[CoCl_2trien]SCN\cdot H_2O$	539 (2.08)	506 (2.32)
cis-α-$[CoClBrtrien]SCN\cdot H_2O$	546 (2.11)	506 (2.34)
cis-α-$[CoBr_2trien]SCN\cdot H_2O$	552 (2.10)	508 (2.40)

Values in parentheses are absorption coefficients.

a) *cis*-$[CoCl_2en_2]SCN$ could not be completely converted into *cis*-$[CoCl(NCS)en_2]Cl$.

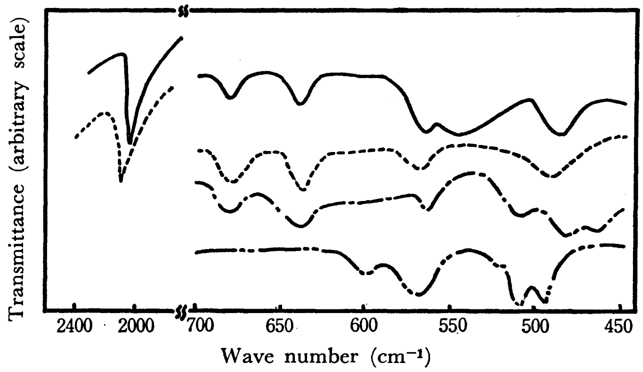

Fig. 2. IR spectra of *cis*-α-$[CoCl_2trien]SCN\cdot H_2O$ (——), its reaction product (······), *cis*-α-$[CoCl_2trien]Cl$ (———) and *cis*-β-$[CoCl_2trien]Cl$ (————).

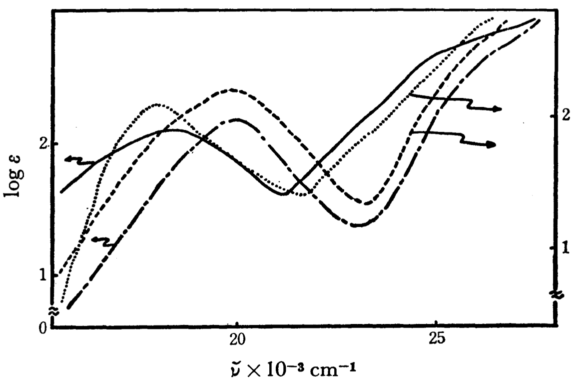

Fig. 3. Absorption spectra of *cis*-$[CoClBren_2]SCN\cdot H_2O$ (——), its reaction product (———), *cis*-$[CoCl(NCS)en_2]Cl$ (----) and *trans*-$[CoCl(NCS)en_2]Br$ (······).

The corresponding trien complexes give a similar pattern to the bis-en complexes in IR spectra before and after the thermal reaction. The IR spectra of *cis*-α-$[CoCl_2trien]SCN\cdot H_2O$, the reaction product, and the related complexes are shown in Fig. 2.

In the far-infrared region, the pattern of the absorption bands originating from the skeletal vibration in each complex does not change much after thermal reaction. There are three geometrical isomers, *cis*-α, cis-β and trans ones, in the octahedral complex involving the trien chelate. The skeletal vibration is more useful in distinguishing these isomers. The configuration of the reaction product of *cis*-α-$[CoCl_2trien]SCN\cdot H_2O$ is considered to be the same as that of the starting complex (Fig. 2). Thus, the ligand-exchange reaction does not involve the stereochemical change, the isomerization from *cis*-α to *cis*-β or *trans*-form.

When two halogen ions in the preheating complex are the same, the chromophore of the reaction product is easily seen. For example, when *cis*-$[CoBr_2en_2]SCN\cdot H_2O$ is heated the product obtained is obviously $[CoBr(NCS)en_2]Br$, but it can not be deduced from only IR data whether Cl^- or Br^- ion is substituted by SCN^- ion upon heating the *cis*-chloro-bromo complex. UV spectra can be used to assign the geometrical isomers and the chromophore of cobalt(III) complexes.[18,19] Numerical values of the absorption maxima of the complexes and their reaction products are shown in Table 2. All the reaction products have absorption maxima at *ca.* 505 nm, and no shoulders at *ca.* 550 nm.

In the chromophore of $[CoX(NCS)(N_4)]$, the first absorption band of *cis*-compound, in general, appears in rather higher frequency than that of *trans*-one. *cis*-$[CoCl(NCS)en_2]Cl$ and *trans*-$[CoCl(NCS)en_2]Br$ were found to exhibit the first absorption maxima at 505 nm and 555 nm, respectively.[20] The absorption spectra of *cis*-$[CoClBren_2]SCN\cdot H_2O$, its reaction product, and the related complexes are given in Fig. 3.

The spectral feature of the reaction product of *cis*-$[CoClBren_2]SCN\cdot H_2O$ is in good agreement with that of *cis*-$[CoCl(NCS)en_2]Cl$. It is therefore concluded that the reaction product from *cis*-$[CoClBren_2]SCN\cdot H_2O$ is *cis*-$[CoCl(NCS)en_2]Br$. Thus, the thiocyanate ion in outer sphere is considered to substitute the coordinated bromide ion but not chloride ion, the *cis*-structure in thermal ligand-exchange reaction being retained. The reaction product from *cis*-$[CoBr_2en_2]SCN\cdot H_2O$, the chromophore of which is $[CoBr(NCS)en_2]$, has a first absorption maxima at 510 nm, and is considered to be *cis*-$[CoBr(NCS)en_2]Br$. This is due to the fact that the ligand field of Cl^- ion is stronger than that of Br^- ion.

Three trien complexes give a similar spectral behavior to that in the bis-en complexes (Table 2). It is concluded that the ligand-exchange reaction proceeds retaining *cis*-form.

Optically active $(-)_D$-*cis*-α-$[CoBr_2trien]SCN\cdot H_2O$ was also used. Apparent difference in activity of the complex was observed before and after the reaction. Their CD and UV spectra are given in Fig. 4.

---

[18] H. Yamatera, This Bulletin, **31**, 95 (1958).

[19] R. A. O. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

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

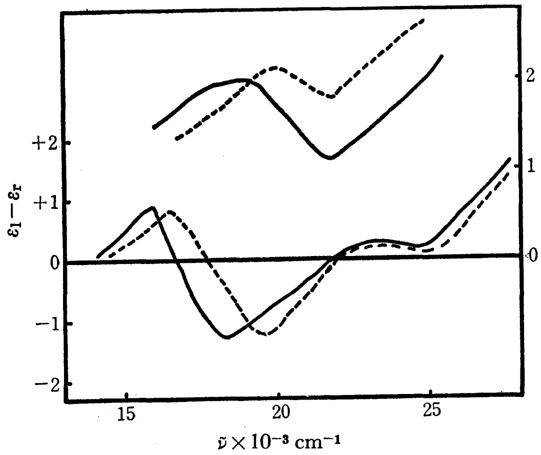

Fig. 4. CD and absorption spectra of $(-)_D$-*cis*-α-$[CoBr_2trien]$-$SCN\cdot H_2O$ (----) and its reaction product (----).

Although the CD spectrum of the reaction product shifts slightly towards the higher frequency side due to the substitution of Br^- by SCN^-, its pattern remains almost unchanged with the same sign even after the reaction. $(+)_D$-*cis*-$[CoCl_2en_2]^+$ and $(+)_{5461}$-*cis*-$[CoCl(NCS)en_2]^+$ have similar CD curves with the same sign, and their absolute configurations are found to be the same, namely, Λ.[21] Complex $(-)_D$-*cis*-α-$[CoBr_2trien]SCN\cdot H_2O$ and its reaction product $(-)_D$-*cis*-α-$[CoBr(NCS)trien]Br$ were found to have the same absolute configuration, since the ring chirality of the trien complex is almost equal to that of bis-en complex. The thermal reaction in the optically active complex is found to accompany neither racemization nor inversion reactions.

It is thus concluded that the thermal ligand-exchange reaction for *cis*-$[CoXY(N_4)]SCN\cdot H_2O$ type complexes proceeds retaining both geometrical and optical configurations giving the formula *cis*-$[CoX(NCS)(N_4)]Y$.

Derivatographic Studies. The derivatograms for the complexes examined are given in Figs. 5, 6 and 7. *cis*-$[CoClBren_2]SCN\cdot H_2O$ and *cis*-$[CoBr_2en_2]SCN\cdot H_2O$ each exhibit a small exothermic peak at *ca.* 125 °C after the appearance of the endothermic peak due to the dehydration in DTA curve (Fig. 5). The exothermic peak corresponds to the ligand-exchange reaction between Br^- ion in the coordination and SCN^- ion in outer sphere as for *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$[10] in which the exchange between the chloride ion and the thiocyanate ion takes place with an exothermic peak.

cis-$[CoCl_2en_2]SCN$ with no lattice water shows no peak in this temperature range, but an exothermic peak overlapping with complicated decomposition peaks at higher temperature. Even upon isothermal heating, it decomposes as soon as the color change begins to appear. At this stage, the C≡N stretching band splits into two peaks at 2040 cm^{-1} and 2100 cm^{-1}. The ligand-exchange reaction does not proceed stoichiometrically for *cis*-$[CoCl_2en_2]SCN$ unlike that for *cis*-$[CoClBren_2]SCN\cdot H_2O$.

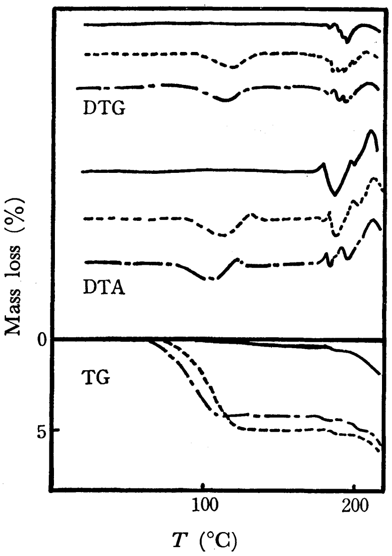

Fig. 5. Derivatograms of *cis*-$[CoCl_2en_2]SCN$ (——), *cis*-$[CoClBren_2]SCN\cdot H_2O$ (----) and *cis*-$[CoBr_2en_2]SCN\cdot H_2O$ (—-—).

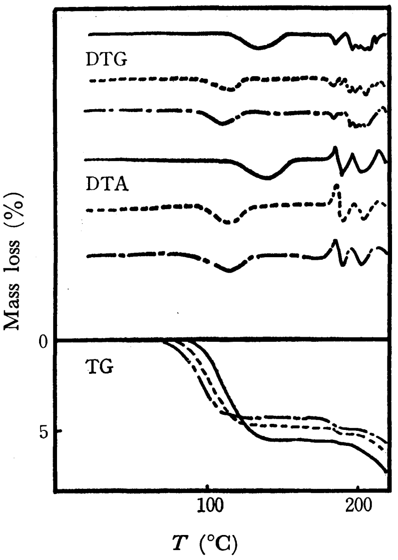

Fig. 6. Derivatograms of *cis*-α-$[CoCl_2trien]SCN\cdot H_2O$ (——), *cis*-α-$[CoClBrtrien]SCN\cdot H_2O$ (----) and *cis*-α-$[CoBr_2trien]$-$SCN\cdot H_2O$ (—-—).

Each derivatogram of the three trien complexes exhibits only one peak attributable to the liberation of lattice water (Fog. 6). The color of the sample changed from violet to brick red after appearance of the endothermic peak, the C≡N stretching band being shifted to 2100 cm^{-1}. The ligand-exchange reaction for the trien complexes might take place in the temperature range of thermal dehydration, since the peak is considered to overlap that of dehydration.

cis-α-$[CoBr_2trien]SCN\cdot H_2O$ readily loses a certain amount of lattice water with no color change on being kept in a vacuum desiccator at room temperature. The derivatogram of this complex exhibits a small exothermic peak at 100 °C due to the lack of a large endothermic peak. This peak appearing with color change could be attributed to the ligand-exchange reaction occurring on heating.

---

[21] T. E. MacDermott, A. M. Sargeson, *Austr. J. Chem.*, **16**, 334 (1963).

TABLE 3. THERMOCHEMICAL FUNCTIONS

Complex	ΔH_d kcal/mol[a)]	$E_a{}^d$ kcal/mol[b)]	ΔH_e kcal/mol[c)]	$E_a{}^e$ kcal/mol[d)]
cis-$[CoClBren_2]SCN\cdot H_2O$	10.8±2.0	26±3	−1.2±1.0	50±5
cis-α-$[CoCl_2trien]SCN\cdot H_2O$	8.6±2.0	33±3		
cis-α-$[CoClBrtrien]SCN\cdot H_2O$	7.8±2.0	31±3		
cis-α-$[CoBr_2trien]SCN\cdot H_2O$	7.2±2.0	30±3		

a) and c) are enthalpy changes of dehydration and ligand-exchange reaction, respectively. b) and d) are activation energies of dehydration and ligand-exchange reaction, respectively.

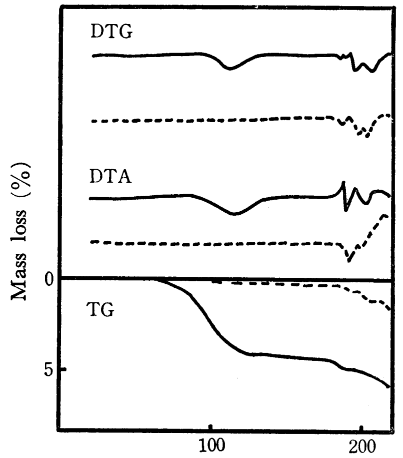

Fig. 7. Derivatograms of $(-)_D$-*cis*-α-$[CoBr_2trien]SCN\cdot H_2O$ (——) and *trans*-$[CoClBren_2]SCN$ (----).

The deviatogram of optically active $(-)_D$-*cis*-α-$[CoBr_2trien]SCN\cdot H_2O$ given in Fig. 7 is similar to that of the corresponding racemic complex. Since all the reaction products indicate the same spectral behavior, it can be concluded that the thermal ligand-exchange reaction occurs just after thermal dehydration.

The following reaction sequence for the *cis*-type complexes is proposed.

(1) *cis*-$[CoXY(N_4)]SCN\cdot H_2O$
$\rightarrow$ *cis*-$[CoXY(N_4)]SCN + H_2O$

(2) *cis*-$[CoXY(N_4)]SCN$
$\rightarrow$ *cis*-$[CoX(NCS)(N_4)]Y$.

In the case of coexistence of Cl^- and Br^- ions in the coordination sphere, the ligand-exchange of Br^- by SCN^- will be more predominant than Cl^-.

On the other hand, the green *trans*-complexes *trans*-$[CoCl_2en_2]SCN$, *trans*-$[CoClBren_2]SCN$ and *trans*-$[CoBr_2en_2]SCN$ have no lattice water, and exhibit no color change on heating. The derivatogram of *trans*-$[CoClBren_2]SCN$ is given in Fig. 7 as an example. In the DTA, DTG and TG curves of this derivatogram, neither the peak for dehydration nor that for the ligand-exchange reaction appears below 185 °C when the complicated thermal decomposition is initiated.

It is understood that the ligand-exchange reaction does not take place in the three dehydrated *trans*-complexes, whereas in the anhydrated *cis*-$[CoCl_2en_2]SCN$ the partial ligand-exchange reaction occurs just before thermal decomposition takes place. This indicates that the configuration of trans isomers should prevent the occurrence of the thermal ligand-exchange reaction.

The thermochemical functions calculated from DTA and DTG curves of the derivatograms are given in Table 3. Because of the incomplete separation of the peaks in DTA curves, no genuine enthalpy changes corresponding to each process of dehydration and ligand-exchange reaction could be calculated separately for *cis*-$[CoClBren_2]SCN\cdot H_2O$, and no DTG and DTA curves of the derivatogram of *cis*-$[CoBr_2en_2]SCN\cdot H_2O$ could be analyzed.

Isothermal Studies. In the isothermal study of *cis*-$[CoClBren_2]SCN\cdot H_2O$, the rate constants of dehydration and ligand-exchange reaction were determined at various temperatures.

Since *cis*-$[CoClBren_2]SCN\cdot H_2O$ and its reaction product *cis*-$[CoCl(NCS)en_2]Br$ have the absorption coefficients 64.9 and 161.8 at 505 nm and 108.5 and 132 at 549 nm in DMSO, respectively, with a 1.0 cm cell, the ratios of the concentration of chloro-bromo/chloro-isothiocyanato complex in the reaction products at a given heating time can be determined spectrophotometrically by means of the equations

$$64.9X + 161.8Y = D_{505}$$

$$108.5X + 132Y = D_{549},$$

where X and Y are the concentrations (in mol^{-1}) of the chloro-bromo and chloro-isothiocyanato complexes, respectively, and D_{505} and D_{549} the absorbances at 505 nm and 549 nm, respectively. The rate constants of the ligand-exchange reaction were calculated from the conversion ratios of the two isomers in each product X/Y. The rate of dehydration was estimated from the weight change of sample with a thermobalance.

The rate constants k_d for dehydration and the rate constants k_e for the ligand-exchange reaction are given in Table 4. The Arrhenius plots of the rate constants are shown in Fig. 8.

The activation energies are (26±1) kcal/mol and (54±2) kcal/mol for dehydration and ligand-exchange reaction, respectively. The values agree with those obtained by analysis of the derivatogram.

TABLE 4. RATE CONSTANTS OF DEHYDRVTION AND LIGAND-EXCHANGE REACTION FOR *cis*-$[CoClBren_2]SCN\cdot H_2O$

T °C	k_d, s^{-1}	T °C	k_e, s^{-1}
95	$7.8\pm0.5\times10^{-6}$	100	$4.0\pm0.3\times10^{-6}$
100.0	$1.1\pm0.3\times10^{-5}$	110.8	$8.9\pm0.5\times10^{-5}$
105	$1.7\pm0.3\times10^{-5}$	121.8	$4.7\pm0.4\times10^{-5}$
108.5	$2.6\pm0.3\times10^{-5}$	131.7	$1.2\pm0.4\times10^{-4}$
111	$3.0\pm0.4\times10^{-5}$		
	$E_a=26\pm2$ kcal/mol		$E_a=54\pm2$ kcal/mol

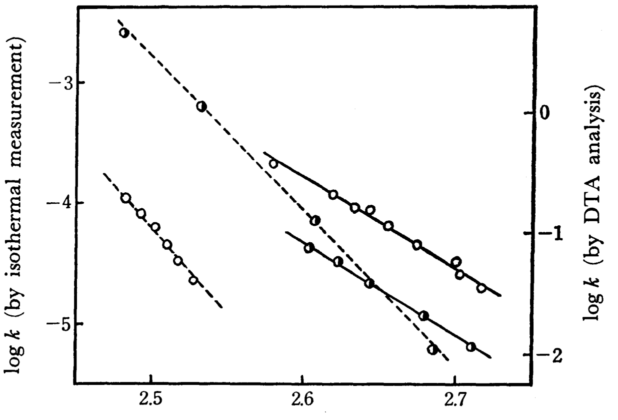

Fig. 8. Arrhenius plots for *cis*-[CoClBren$_2$]SCN·H$_2$O in the dehydration (——) and ligand-exchange reaction (----) by DTA analysis (○) and isothermal measurement (◑).

If the thermal reaction in a solid phase proceeds through the aquation-anation pathway, the activation energy of the thermal reaction will be nearly equal to that of dehydration, and if the reaction proceeds by intramolecular mechanism, the activation energy would be comparatively higher than that by aquation-anation mechanism.

In the study of *cis*-[CoClBren$_2$]SCN·H$_2$O, the two Arrhenius plots for dehydration and the ligand-exchange reaction were not parallel with each other (Fig. 8), and the activation energy of the ligand-exchange reaction was considerably higher than that of dehydration. It is assumed that the lattice water plays no important role in the ligand-exchange reaction.

The ligand-exchange reaction occurs after dehydration and thus proceeds *via* the intramolecular mechanism. All the reaction products of *cis*-[CoXY(N$_4$)]-SCN·H$_2$O type complexes were of *cis*-structure with respect to a halogen ion originally coordinated and an isothiocyanate ion entering the coordination sphere.

When *cis*-[CoClBren$_2$]SCN·H$_2$O and CuSO$_4$·5H$_2$O separately placed in a sealed tube were heated, the reaction product of the former differed from that obtained in an open system, *viz.*, it was a mixture of *cis*- and *trans*-[CoCl(NCS)en$_2$]Br. In such a closed system, the gaseous water molecule evolving from the sample and CuSO$_4$·5H$_2$O can not escape from the reaction system, and may aquate the complex catalytically at the solid surface. The thermal reaction might proceed through the aquation-anation pathway accompanied by the stereochemical change, isomerization from *cis* to *trans*-form.

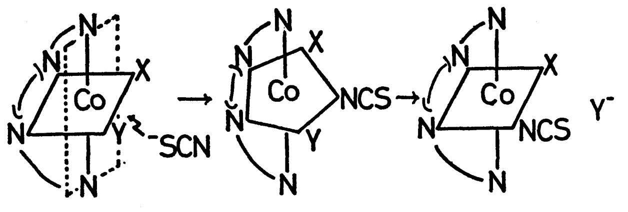

Fig. 9. Probable reaction mechanism.

The following reaction mechanism for the ligand-exchange reaction of *cis*-[CoXY(N$_4$)]SCN·H$_2$O type complex in the solid phase is postulated (Fig. 9).

The thiocyanate ion would attack at a position *cis* to the two halogen ions coordinated to form the seven coordinated reaction intermediates and then one of the halogen ions would be removed to outer coordination sphere. In the case of the coexistence of Cl$^-$ and Br$^-$ ions in the coordination, the Co–Br bond breaking takes place after making the seven coordinated intermediate, since the Co–Br bond energy is considered to be smaller than the Co–Cl one.

The thermal reaction products through this pathway should be of *cis*-structure without any stereochemical change such as racemization or an inversion in the optically active complex. The exchange reaction and isomerization from *cis,trans*-[CoCl$_2$(NH$_3$)$_2$en]SCN·H$_2$O to *cis,cis*-[CoCl(NCS)(NH$_3$)$_2$en]Cl occurred simultaneously, where the thiocyanate ion in outer sphere attacked at a position trans to the two halogen ions. In the case of *cis*-[CoXY(N$_4$)]SCN·H$_2$O, however, the chelate ring of ethylenediamine or triethylenetetramine might prevent the thiocyanate ion from attacking the trans site and make the *cis*-attack more easily. After the liberation of water molecule from the crystal lattice upon heating, packing may somewhat loosen as in an amorphous substance.

The looseness would affect the acceleration of the mobility of the thiocyanate ion in the solid phase. The assumption seems plausible, since the monohydrated *cis*-complexes exhibit a perfect ligand-exchange after dehydration, while the other anhydrous *cis*-[CoCl$_2$en$_2$]SCN showed only partial ligand-exchange just before thermal decomposition.