Thermal Reaction in a Series of Ammineisothiocyanatochromium(III) Complexes in Solid State.[1]

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The thermal decomposition of $[Cr(NH_3)_6](SCN)_3$, $[Cr(NCS)(NH_3)_5](SCN)_2$ and *cis*-$[Cr(NCS)_2(NH_3)_4]SCN$ in solid state was studied by isothermal as well as continuous temperature-rise methods. Under isothermal heating at 140 °C, $[Cr(NH_3)_6](SCN)_3$ changed stepwise to *cis,trans*-$[Cr(NCS)_3(NH_3)_3]$ through *trans*-$[Cr(NCS)_2(NH_3)_4]$-SCN, $[Cr(NCS)(NH_3)_5](SCN)_2$ turning to the *cis-trans* complex over the *trans* complex in the same manner as $[Cr(NH_3)_6](SCN)_3$. Under the continuous temperature-rise, $[Cr(NH_3)_6](SCN)_3$, $[Cr(NCS)(NH_3)_5](SCN)_2$ as well as *trans*-$[Cr(NCS)_2(NH_3)_4]SCN$ were found to be directly converted into *cis,trans*-$[Cr(NCS)_3(NH_3)_3]$.

The thermal decomposition of various chromium(III) compiexes has been extensively investigated.[2] As regard the thermal decomposition of several hexaamminechromium(III) halides, Wendlandt and Chou[3] reported that decomposition is initiated by the substitution reaction of a coordinated ammonia by halide ion in outer sphere, but gave no discussion on the structure of the decomposition products. Tanaka and Nagase carried out kinetic studies of the thermal decomposition reaction of $[Cr(NH_3)_6]Cl_3$, $[CrCl(NH_3)_5]Cl_2$, and *cis*-$[CrCl_2(NH_3)_4]Cl$ in solid state,[4] and proposed the following possible pathway for the deamminationanation reaction of these chromium(III) ammine complexes:

$$[Cr(NH_3)_6]Cl_3 \downarrow [CrCl(NH_3)_5]Cl_2 \downarrow \textit{trans}\text{-}[CrCl_2(NH_3)_4]Cl \overset{\text{isomerization}}{\rightleftharpoons} \textit{cis}\text{-}[CrCl_2(NH_3)_4]Cl \downarrow \textit{cis, trans}\text{-}[CrCl_3(NH_3)_3] \overset{\text{isomerization}}{\longleftarrow} \textit{cis, cis}\text{-}[CrCl_3(NH_3)_3]$$

Recently, they made it clear that *trans*-$[CrCl_2(NH_3)_4]Cl$ is reversibly isomerized to the corresponding *cis*-form.[5]

So far systematic pathways for the thermal decomposition of the chromium(III) ammine isothiocyanato complexes are not known. Werner and Halben[6] obtained a pale rose insoluble product $[Cr(NCS)_3(NH_3)_3]$ by isothermal heating of $[Cr(NCS)(NH_3)_5](SCN)_2$ at 130—140 °C, but its geometrical structure has not been identified.

In order to examine the structural changes along with the thermal reaction pathways of the ammine chromium(III) thiocyanate, we have studied the decomposition reactions of $[Cr(NH_3)_6](SCN)_3$, $[Cr(NCS).(NH_3)_5](SCN)_2$, and *cis*-$[Cr(NCS)_2(NH_3)_4]SCN$ in solid state by the isothermal and the continuous temperature-rise methods. The structures of the decomposition products obtained upon heating were clarified by the measurement of their infrared and electronic spectra. Possible reaction pathways in the thermal reaction of these chromium(III) ammine complexes were proposed.

Experimental

Preparation of Complexes. Hexaamminechromium(III) thiocyanate, $[Cr(NH_3)_6](SCN)_3$, was prepared by adding potassium thiocyanate to the corresponding chloride obtained by the method in literature.[7]

Isothiocyanatopentaamminechromium(III) thiocyanate, $[Cr(NCS)(NH_3)_5](SCN)_2$, and *cis*-diisothiocyanatotetraamminechromium(III) thiocyanate, *cis*-$[Cr(NCS)_2(NH_3)_4]$-SCN, were prepared by the method given by Werner and Halben[6] and by Kyuno *et al.*[8] All the complexes were identified by elemental analysis and absorption spectral measurement.

trans-Diisothiocyanatotetraamminechromium(III) thiocyanate, *trans*-$[Cr(NCS)_2(NH_3)_4]SCN$, was prepared by the isothermal heating of $[Cr(NH_3)_6](SCN)_3$ at 140 °C for 10 min.

cis, trans-Triisothiocyanatotriamminechromium(III), *cis, trans*-$[Cr(NCS)_3(NH_3)_3]$, was prepared by the isothermal heating of $[Cr(NH_3)_6](SCN)_3$ at 140 °C for seven hours and was prepared by the known method.[6]

Isothermal Measurement. Isothermal measurement for these complexes was carried out in a Toyo Roshi Air Oven, the temperature of the sample being controlled within ± 1 °C at 140 °C. In each run a 500 mg sample smaller than 200 mesh in size was weighed.

Continuous Temperature-rise Measurement. The continuous temperature-rise measurement was carried out with a Metrimpex Derivatograph Type-OD-102 and a Tokyo Koki thermobalance. Derivatographic measurement was made in a nitrogen stream under heating rate of 1 °C/min, 500 mg of the sample being used in each run. TG curve was obtained with the thermobalance in an open system under the heating rate of 1 °C/min for 500 mg of the sample. The results obtained by the above two instruments were in good agreement with each other.

Apparatus for Measurement. Molar conductivity, electronic and IR absorption spectra and X-ray diffraction were measured with a Yanagimoto conductivity-measuring equipment, a Hitachi EPU-2A spectrophotometer, a JASCO IR spectrophotometer DS-301 and with a Toshiba EO-60B X-ray Analyser, respectively.

Results and Discussion

Thermal Reaction of $[Cr(NH_3)_6](SCN)_3$ under Isothermal Heating at 140±1 °C. The starting yellow complex liberated two moles of ammonia in the initial stage of 10 min heating, turning to reddish orange. The molar conductivity of the product in a 5×10^{-3} M aqueous

Table 1. IR spectral bands of ammine-isothiocyanato chromium(III) complexes

	ν_{CH}	$\delta_{\alpha NH_3}$	δ_{SNH_3}	ρ_{NH_3}
$[Cr(NH_3)_6(SCN)_3]$	2050	1600	1310	766
$[Cr(NCS)(NH_3)_5](SCN)_2$	2050	1605	1290	730
cis-$[Cr(NCS)_2(NH_3)_4]SCN$	2080	1607	1292	720
$[Cr(NCS)_2(NH_3)_4]SCN$[a]	2050	1588	1263	722
$[Cr(NCS)_3(NH_3)_3]$	2050[b]	1599[b]	1270[b]	722[b]

δ_α: degenerate deformation, δ_S: symmetric deformation, ρ: rocking

a) Obtained from $[Cr(NH_3)_6](SCN)_3$ by isothermal heating. b) These values were in agreement with those obtained from $[Cr(NH_3)_6](SCN_3)$ by the continuous temperature-rise method.

solution was 125 ohm^{-1} cm^2/mol. This value corresponds to that of 1:1 valency type complex. Found: N, 33.13; C, 12.07; H, 4.06%. Calcd for $[Cr(NCS)_2(NH_3)_4]SCN$: N, 33.01; C, 12.24; H, 4.11%. The product is soluble in acetone, differing from *cis*-$[Cr(NCS)_2(NH_3)_4]SCN$ insoluble.

The wave numbers of some IR spectral bands are listed in Table 1 for the ammine-isothiocyanato chromium(III) complexes. We see that the thermal reaction product $[Cr(NCS)_2(NH_3)_4]SCN$ gives the absorption band assigned to the NH_3 symmetric deformation vibration at 1263 cm^{-1}, while the corresponding *cis*-form complex gives the corresponding band at 1292 cm^{-1}. The X-ray diffraction pattern of this compound was found to differ from that of *cis*-$[Cr(NCS)_2(NH_3)_4]SCN$.

The electronic spectral data of a series of ammine-isothiocyanato chromium(III) complexes are shown in

Table 2. Absorption maxima of chromium(III) complexes

	ν_1 (logε)	ν_2 (logε)	ν_3 (logε)
$[Cr(NH_3)_6](SCN)_3$	21.6 (1.65)	28.5 (1.58)	
$[Cr(NCS)(NH_3)_5](SCN)_2$	20.4 (1.87)	27.1 (1.69)	33.8 (3.43)
cis-$[Cr(NCS)_2(NH_3)_4]SCN$	20.2 (1.93)	26.9 (1.72)	33.1 (3.71)
$[Cr(NCS)_2(NH_3)_4]SCN$[a]	19.9 (1.93)	26.5 (1.85)	33.2 (3.72)
$[Cr(NCS)_2(NH_3)_4]SCN$[b]	19.9 (1.95)	26.5 (1.85)	33.2 (3.75)
$[Cr(NCS)_3(NH_3)_3]$[a]	19.3 (2.04)	25.5 (1.95)	30.9 (3.84)
$[Cr(NCS)_3(NH_3)_3]$[c]	19.3 (2.04)	25.5 (1.95)	30.9 (3.84)
$[Cr(NCS)_3(NH_3)_3]$[b]	19.3 (2.02)	25.5 (1.96)	30.9 (3.82)
$[Cr(NCS)_3(NH_3)_3]$[d]	19.3 (2.02)	25.5 (1.96)	30.8 (3.82)
$[Cr(NCS)_3(NH_3)_3]$[e]	19.3 (2.02)	25.5 (1.97)	30.8 (3.84)

a) obtained from $[Cr(NH_3)_6](SCN)_3$ by isothermal heating. b) obtained from $[Cr(NCS)(NH_2)_5](SCN)_2$ by isothermal heating. c) obtained from $[Cr(NH_3)_6](SCN)_3$ by continuous temperature-rise method. d) obtained from $[Cr(NCS)(NH_3)_5](SCN)_2$ by the continuous temperature-rise method. e) obtained from a) by the continuous temperature-rise method.

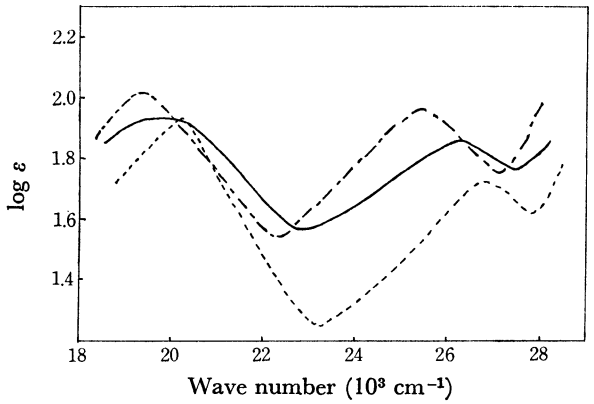


Fig. 1. The electronic spectra of $[Cr(NCS)_2(NH_3)_4]SCN$ (——) and $[Cr(NCS)_3(NH_3)_3]$ (– – –) obtained from $[Cr(NH_3)_6](SCN)_3$ by the isothermal heating along with that of cis-$[Cr(NCS)_2(NH_3)_4]$ SCN (------).

Table 2. The spectra of $[Cr(NCS)_2(NH_3)_4]SCN$ and $[Cr(NCS)_3(NH_3)_3]$, obtained by the isothermal heating of $[Cr(NH_3)_6](SCN)_3$ are given in Fig. 1 together with that of *cis*-$[Cr(NCS)_2(NH_3)_4]SCN$. It is seen that the spectra of $[Cr(NCS)_2(NH_3)_4]SCN$ specimens obtained from $[Cr(NH_3)_6](SCN)_3$ and $[Cr(NCS)(NH_3)_5](SCN)_2$ are in complete agreement with each other, and that they differ from the spectrum of *cis*-$[Cr(NCS)_2(NH_3)_4]SCN$.

It is concluded that the geometrical configuration of the thermal product formed by liberating two moles of ammonia from $[Cr(NH_3)_6](SCN)_3$ is *trans*-$[Cr(NCS)_2(NH_3)_4]SCN$.

The starting hexaammine complex liberated three moles of ammonia after seven hours heating with a color change to reddish purple. The product is soluble in acetone but not in water. Found: N, 30.67; C, 12.63; H, 3.34%. Calcd for $[Cr(NCS)_3(NH_3)_3]$: N, 30.30; C, 12.99; H, 3.25%. No composition change

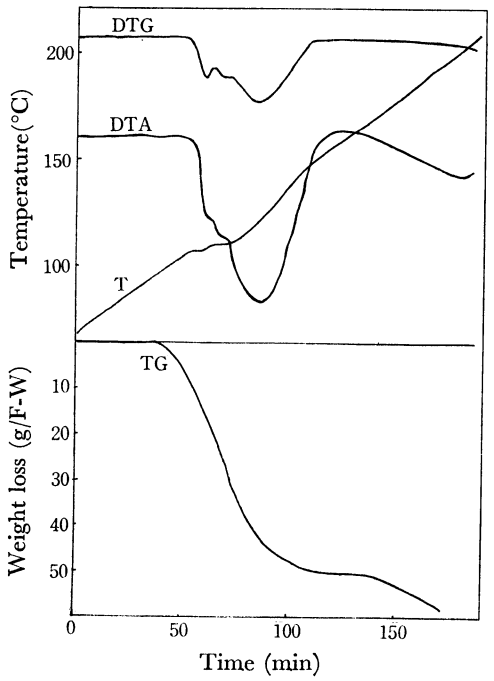


Fig. 2. The derivatogram for $[Cr(NH_3)_6](SCN)_3$.

took place even after heating for 11 hr. As the geometrical isomers of this product, either *cis-trans* or *cis-cis* configuration is possible. However, since the product at the first thermal decomposition step has a *trans*-configuration, it is likely that the product at the second step is *cis,trans*-$[Cr(NCS)_3(NH_3)_3]$. It is reasonable to consider that the *cis,cis*-configuration is less stable than the *cis,trans* one from the viewpoint of the steric hindrance, as has been reported by Tanaka and Nagase.[4]

Thermal Reaction of $[Cr(NH_3)_6](SCN)_3$ *under Continuous Temperature-rise.* The derivatogram of $[Cr(NH_3)_6](SCN)_3$ is shown in Fig. 2. The TG curve shows that the weight loss starts at 110 °C, and the weight remains almost constant untill 170 °C. The DTA curve gives an endothermic peak with two shoulders. The DTG curve also shows a similar feature to that of the DTA curve. The weight loss in the TG curve corresponds to the loss of three moles of ammonia. The analytical data of the product are as follows: Found: N, 29.68; C, 12.61; H, 3.33%. Calcd for $[Cr(NCS)_3(NH_3)_3]$: N, 30.30; C, 12.99; H, 3.25%.

The data listed in Tables 1 and 2 support the view that the product has *cis,trans*-configuration. It is obvious from the spectral data that *cis,trans*-$[Cr(NCS)_3(NH_3)_3]$ produced in the derivatograph is identical with the final product obtained by isothermal heating at 140 °C. The X-ray diffraction pattern also supports this conclusion. The shoulders and the peak in DTA can be attributed to the liberation of one and two moles of ammonia from the starting material, respectively. However, it can not be confirmed whether $[Cr(NCS)(NH_3)_5](SCN)_2$ is formed in the intermediate step or not.

Thermal Reaction of $[Cr(NCS)(NH_3)_5](SCN)_2$ *under Isothermal Heating at 140±1 °C.* The starting complex seems to change to *trans*-$[Cr(NCS)_2(NH_3)_4]SCN$ after eight minutes heating and finally to *cis,trans*-$[Cr(NCS)_3(NH_3)_3]$ as judged by the weight loss. But the stoichiometry was not complete. Even after 18 hr heating, the weight loss amounted to only 98% of two moles of ammonia. Werner and Halben[6] reported that $[Cr(NCS)_3(NH_3)_3]$ was obtained from $[Cr(NCS)(NH_3)_5](SCN)_2$ by isothermal heating (at 130—140 °C) for 30—40 hr. The results we obtained are not contradictory to theirs.

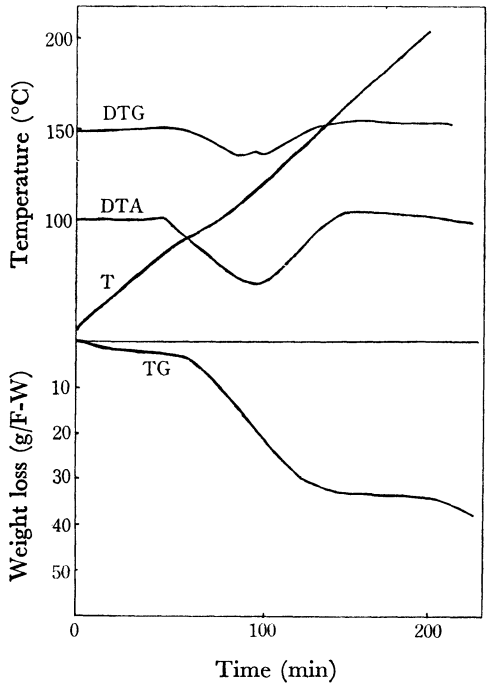


Fig. 3. The derivatogram for $[Cr(NCS)(NH_3)_5](SCN)_2$.

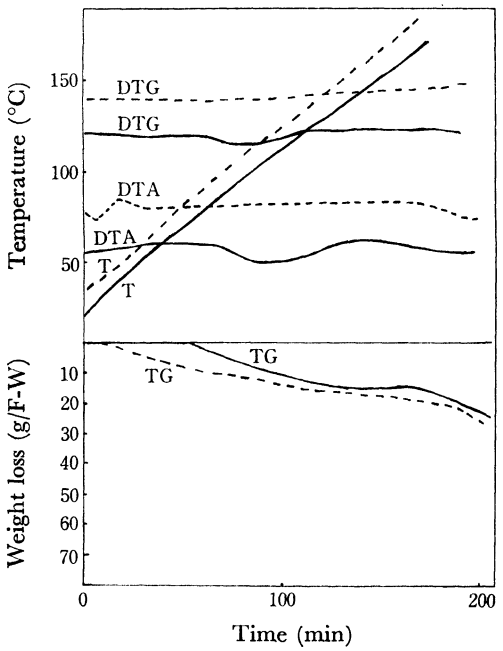
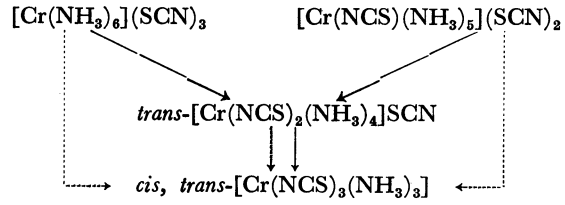


Fig. 4. The derivatograms for *trans*-$[Cr(NCS)_2(NH_3)_4]SCN$ obtained from $[Cr(NH_3)_6](SCN)_3$ by the isothermal heating (——) and *cis*-$[Cr(NCS)_2(NH_3)_4]SCN$ (------).

Thermal Reaction of $[Cr(NCS)(NH_3)_5](SCN)_2$ *under Continuous Temperature-rise.* The derivatogram of this complex is shown in Fig. 3. The TG, DTA, and DTG curves support an endothermal reaction one step. The weight loss corresponds to only 90% of two moles of ammonia. The result suggests that the reaction in the derivatograph is not completely stoichiometric and is similar to the isothermal reaction. The main product was confirmed to have a *cis,trans*-configuration from the spectral measurements.

Thermal Reaction of trans- *and* cis-$[Cr(NCS)_2(NH_3)_4]SCN$ *under Continuous Temperature-rise.* The derivatograms of these complexes are shown in Fig. 4. The thermal product obtained from the *trans* complex was identified by electronic spectra to be *cis,trans*-$[Cr(NCS)_3(NH_3)_3]$, whereas the configuration of the product obtained from the *cis* complex was difficult to be determined. For the *cis* complex, the derivatogram showed no distinct plateau corresponding to the weight loss of one mole of ammonia. The product obtained at the heating step by the thermobalance was not pure due to its hygroscopic character. The decomposition process of the *cis* complex must be a complicated one and the isomerization could not be clearly observed in both the isothermal measurement as well as the con-



(——) The isothermal reaction (at 140°±1°C)
(------) The continuous temperature-rising reaction (1 °C/min)

Fig. 5. The possible reaction processes of isothiocyanato-ammine chromium(III) complexes.

tinuous temperature-rise method. The results differ remarkably from those in the decomposition processes of *cis*-$[CrCl_2(NH_3)_4]Cl$ reported by Tanaka and Nagase.[4]

Possible decomposition reaction processes of a series of isothiocyanato-ammine chromium(III) complexes can be represented as shown in Fig. 5.

References

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