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Cis-to-Trans Isomerization of Bis(diamine)bis(isothiocyanato)chromium(III) Thiocyanate in the Solid State

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Solid-state thermal reactions of *trans*- and *cis*-$[Cr(NCS)_2(AA)_2]SCN$ where AA is 1,2-ethanediamine (en) or 1,3-propanediamine (tn) were studied. Upon heating, both the cis- and trans-complexes lost half mole of diamine to convert into the double complex *trans*-$[Cr(NCS)_2(AA)_2][Cr(NCS)_4(AA)]$. The anion moiety $[Cr(NCS)_4(AA)]^-$ was isolated from the double complex. The thermal reactions are thus useful for easy preparation of $[Cr(NCS)_4(AA)]^-$complex, which has previously been obtained with difficulty from solution reactions.

In 1904, Pfeiffer et al. reported the solid state deamination of the tris(1,2-ethanediamine) complex $[Cr(en)_3]X_3$ ($X=Cl^-$ or NCS^-).[1] The complex, when heated, deaminated to form *cis*-$[CrCl_2(en)_2]Cl$ or *trans*-$[Cr(NCS)_2(en)_2]SCN$. Until recently, the above deamination has been used as the standard procedures for synthesizing a series of *cis*- and *trans*-bis(diamine) complexes.[2] We recently investigated in detail the deamination of a complete series of tris(diamine) complexes: $[Cr(AA)_3]X_3$, $[Cr(AA)_2(BB)]X_3$, and $[Cr(AA)(BB)(CC)]X_3$ where AA, BB, and CC denote different diamines, and X is a halide ion.[3] We noticed that the bis(diamine)complexes obtained by the deamination sometimes undergo subsequent isomerization. Then, we studied the effect of various diamines and anions on the isomerization.[4,5] The solid-state thermal reaction of bis(diamine)bis(isothiocyanato)chromium(III) thiocyanates has never been approached. In this paper, we describe the behavior of the solid *cis*- and *trans*-$[Cr(NCS)_2(AA)_2]SCN$ when heated non-isothermally in open dynamic condition, where AA is 1,2-ethanediamine or 1,3-propanediamine; the former can form a five-membered chelate ring and the latter, a six-membered chelate ring with chromium(III) ion.

Experimental

Preparation of Complexes. *trans*-$[Cr(NCS)_2(en)_2]SCN$ (**1**) was prepared according to the known method.[3] *cis*-$[Cr(NCS)_2(en)_2]SCN$ (**2**), *trans*-$[Cr(NCS)_2(tn)_2]SCN$ (**3**), and *cis*-$[Cr(NCS)_2(tn)_2]SCN\cdot H_2O$ (**4**) were obtained by the metatheses from the corresponding chloro-chloride[6,7] and KSCN as reported previously.[3]

Non-Isothermal Measurements. Thermal reactions of the samples were recorded on SEIKO SSC/580 TG/DTA-30 and SSC/580 DSC/10 thermal analysers in a nitrogen atmosphere (flow rate: 200 cm^3 min^{-1}). All the measurements were carried out at the heating rate of 2 °C min^{-1}. About 15 mg of the samples was used for TG/DTA and about 10 mg, for DSC.

Spectral Measurements. Visible spectra of the samples were measured with a JASCO UVIDEC 505 spectrophotometer. IR spectra were obtained by a KBr method with a JASCO A-3 infrared spectrophotometer.

TLC. The presence of a single species in the deaminated products was confirmed by TLC. The plates used were those of silica gel 60F-254 made by Merck Ltd.

Molar Conductivities. Molar conductivities were measured in acetone at 25 °C to determine the charges of the samples using a Yokogawa Universal Bridge TYPE BU-Z-13A.

Purification of Products Obtained by Deamination. *trans*-$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$(**5**). One gram of finely powdered complex [**1** or **2**] was spread in a thin layer on a watch glass and heated in an air oven [heating conditions: 200—205 °C (2 h) for **1** and 195—200 °C (5 h) for **2**]. The product thus obtained was throughly washed with boiling water (250 cm^3), cold water, ethanol, and ether, and recrystallized from a mixture of acetone-water (4 : 1). Pink flaky crystals thus obtained were collected by filtration and air dried. Yield 80%.

trans-$[Cr(NCS)_2(tn)_2][Cr(NCS)_4(tn)]$ (**6**). The complex was prepared by the same method as that described for **5**. In this case, either the complex **3** or **4** was taken as the starting material [heating conditions: 195—200 °C (5 h) for **3** and 195—200 °C (3 h) for **4**]. This complex appears as red-pink crystals. Yield 80%.

Results

Thermal Reactions under Non-Isothermal Conditions. Figure 1 shows the TGA and DSC curves for the complexes **1** and **2**. As seen from the TG curve of the complex *trans*-$[Cr(NCS)_2(en)_2]SCN\cdot H_2O$ (**1**), it is dehydrated at 38 °C followed by the evolution of half mole of en at 181—254.5 °C and then a clear plateau is obtained. The complex changed in color from yellowish orange to pink due to the formation of the double complex *trans*-$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$. The corresponding DSC curve shows two endothermic peaks for the elimination of diamine. The complex *cis*-$[Cr(NCS)_2(en)_2]SCN$ (**2**) deaminates at 183.5 °C and is transformed to the double complex *trans*-$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$ quantitatively at 250 °C. For this reaction, the DSC curve shows a series of endo- and exothermic peaks (Fig. 1). It is interesting to note that during deamination, the complex undergoes cis-to-trans isomerization. Similar results were observed in case of the 1,3-propanediamine complexes. The complex *trans*-$[Cr(NCS)_2(tn)_2]SCN$ (**3**) undergoes deamination at 170—243 °C and a clear plateau is obtained in the TG curve (Fig. 2). The weight loss corresponds

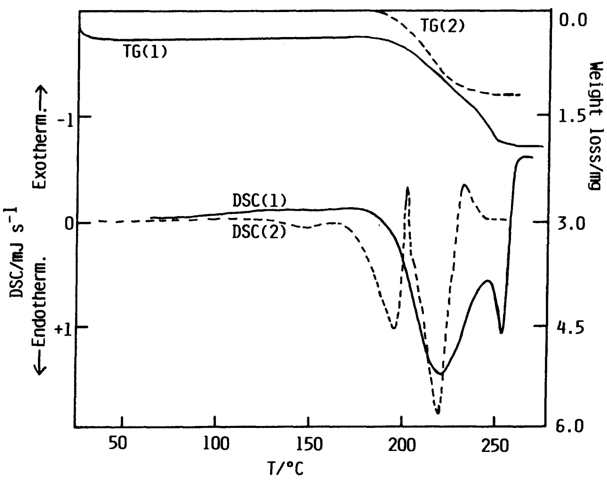

Fig. 1. TG and DSC curves of *trans*-[$Cr(NCS)_2(en)_2$]SCN·H_2O (**1**) (——) and *cis*-[$Cr(NCS)_2(en)_2$]SCN (**2**) (----). Sample weights: for TG, **1**, 18.45 mg, **2**, 13.90 mg; for DSC, **1**, 8.40 mg, **2**, 9.80 mg. (Endothermic DSC peak for the dehydration of **1** is not shown because the compound started dehydration during grinding at ambient temperature).

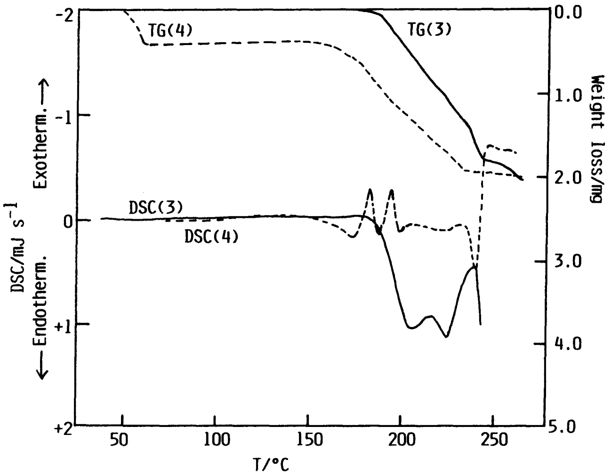

Fig. 2. TG and DSC curves of *trans*-[$Cr(NCS)_2(tn)_2$]SCN (**3**) (——) and *cis*-[$Cr(NCS)_2(tn)_2$]SCN·H_2O (**4**) (----). Sample weights: for TG, **3**, 17.50 mg, **4**, 18.80 mg; for DSC, **3**, 9.70 mg, **4**, 9.58 mg. (Endothermic DSC peak for the dehydration of **4** is not shown because the compound started dehydration during grinding at ambient temperature).

to 0.5 mol of the diamine. The corresponding DSC curve shows two endothermic peaks. In case of *cis*-[$Cr(NCS)_2(tn)_2$]SCN·H_2O (**4**) (Fig. 2), dehydration starts at 42 °C and anhydrous weight level is attained at 64 °C. As the temperature is raised further, it begins to lose the diamine (146—234 °C) showing a series of endo- and exothermic DSC peaks leaving a stable double complex *trans*-[$Cr(NCS)_2(tn)_2$][$Cr(NCS)_4(tn)$]. Like the 1,2-ethanediamine complex, cis-to-trans isomerization also takes place along with deamination. The following schemes summarize the solid state reactions:

$$2\ \textit{trans}\text{-}[Cr(NCS)_2(AA)_2]SCN \xrightarrow[\Delta]{-(AA)} \textit{trans}\text{-}[Cr(NCS)_2(AA)_2][Cr(SCN)_4(AA)]$$

$$2\ \textit{cis}\text{-}[Cr(NCS)_2(AA)_2]SCN \xrightarrow[\Delta]{-(AA)} \textit{trans}\text{-}[Cr(NCS)_2(AA)_2][Cr(SCN)_4(AA)]$$

Characterization of Complexes 5 and 6. The presence of complex cation and anion in the double complexes **5** and **6** was convincingly demonstrated by the following ion exchange experiments: A concentrated solution of **5** or **6** in acetone-water(3 : 2) mixture [addition of more water causes precipitation of the complex] was passed through a Dowex 1-X8 anion exchanger in Cl^- form (20×1.5 cm) and the cations were eluted with one column volume of acetone-water (3 : 2) mixture. The effluents were orange in color and the upper part of the resins turned red-violet due to the retention of the complex anion. The effluents were quickly concentrated in a rotoevaporator at room temperature and thereto excess NH_4SCN was added. Yellowish orange [in case of **5**] and reddish orange [in case of **6**] crystals of *trans*-[$Cr(NCS)_2(AA)_2$]SCN separated out on standing. The IR and electronic spectra (350—700 nm) of these products were identical with those of *trans*-[$Cr(NCS)_2(en)_2$]SCN·H_2O (**1**) and *trans*-[$Cr(NCS)_2(tn)_2$]SCN (**3**) respectively. For the isolation of complex anions, similar exchange experiments were performed utilizing the cation exchanger Amberlite IR-120B (Na^+ form). In these cases, red-violet effluents were obtained and the resins were turned orange due to the retention of the complex cation. From these effluents the anionic complexes were precipitated out by adding tetraethylammonium bromide (Et_4NBr). These products were recrystallized from acetone-water (1 : 1) mixture. [Et_4N][$Cr(NCS)_4(en)$] and [Et_4N][$Cr(NCS)_4(tn)$] were obtained as red-violet and red-purple crystals, respectively. All the compounds were characterized by analytical data (Table 1), DSC and TG measurements, electronic and IR data (Table 2), molar conductivities and TLC data (Table 3). Although *cis*- and *trans*-[$Cr(NCS)_2(AA)_2$]SCN exhibit similar absorption maxima in their visible electronic spectra, they can be easily distinguished from thier molar absorbances (Table 2). As the trans-complexes are much more symmetrical (D_{4h}) than the cis-complexes (C_{2v}), the former shows much lower molar absorbances than the latter in their visible absorption spectra.

The double complexes obtained from *cis*- and *trans*-[$Cr(NCS)_2(AA)_2$]SCN possess exactly similar IR, electronic spectra (350—700 nm), molar conductivities and TLC data. We also separated the cationic and anionic parts by ion exchange chromatography from both the double complexes synthesized from *cis*- and *trans*-[$Cr(NCS)_2(AA)_2$]SCN. In both the cases identical prod-

Table 1. Analytical Data for the Complexes Obtained

Complex	H(%)		C(%)		N(%)	
	Found	Calcd	Found	Calcd	Found	Calcd
trans-$[Cr(NCS)_2(en)_2]SCN$[a]	4.67	4.65	24.15	24.26	28.18	28.30
cis-$[Cr(NCS)_2(en)_2]SCN$	4.61	4.65	24.05	24.26	28.14	28.30
trans-$[Cr(NCS)_2(tn)_2]SCN$	5.35	5.38	28.79	28.86	26.26	26.18
cis-$[Cr(NCS)_2(tn)_2]SCN \cdot H_2O$	5.55	5.64	27.57	27.54	25.10	24.98
$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$[b]	3.91	3.82	23.14	22.77	26.26	26.56
$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$[c]	3.98	3.82	22.75	22.77	26.34	26.56
$[Cr(NCS)_2(tn)_2][Cr(NCS)_4(tn)]$[d]	4.55	4.48	26.67	26.69	24.89	24.90
$[Cr(NCS)_2(tn)_2][Cr(NCS)_4(tn)]$[e]	4.48	4.48	26.70	26.69	24.69	24.90
$[Et_4N][Cr(NCS)_4(en)]$	5.88	5.94	35.27	35.42	20.37	20.65
$[Et_4N][Cr(NCS)_4(tn)]$	6.25	6.18	36.76	36.86	19.76	20.06

a) Analyzed in anhydrous form. b) Synthesized from *trans*-$[Cr(NCS)_2(en)_2]SCN$. c) Synthesized from *cis*-$[Cr(NCS)_2(en)_2]SCN$. d) Synthesized from *trans*-$[Cr(NCS)_2(tn)_2]SCN$. e) Synthesized from *cis*-$[Cr(NCS)_2(tn)_2]SCN$.

Table 2. IR and Electronic Spectral Data for the Complexes

No.	Complex	IR data $\tilde{\nu}(CN)$[a]$/cm^{-1}$	Electronic spectral data nm ($\varepsilon/mol^{-1}\,dm^3\,cm^{-1}$)
1	*trans*-$[Cr(NCS)_2(en)_2]SCN \cdot H_2O$	2090vs, 2064sh[b]	488(79.5), 364(60.3)[e]
2	*cis*-$[Cr(NCS)_2(en)_2]SCN$	2098vs, 2083vs, 2061s[b]	485(147), 371(88.2)[e]
3	*trans*-$[Cr(NCS)_2(tn)_2]SCN$	2083vs, 2064sh[b]	496(88.9), 370(71.9)[e]
4	*cis*-$[Cr(NCS)_2(tn)_2]SCN \cdot H_2O$	2117vs, 2092vs, 2059vs[b]	488(104.5), 370(72.9)[e]
5	*trans*-$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$[c]	2124sh, 2102sh, 2086vs, 2076sh	510(109.1), 389(84.6)[f]
6	*trans*-$[Cr(NCS)_2(tn)_2][Cr(NCS)_4(tn)]$[d]	2118s, 2088vs, 2074vs, 2060vs	515(103.8), 388(84.3)[f]
7	$[Et_4N][Cr(NCS)_4(en)]$	2017s, 2100sh, 2088vs, 2076sh	525(146.4), 398(109.9)[f]
8	$[Et_4N][Cr(NCS)_4(tn)]$	2123s, 2103sh, 2092vs, 2077vs	525(130.1), 395(114.9)[f]

a) Assignment of ν(CS) and δ(NCS) are difficult due to the presence of ligand bands. b) Due to ionic SCN group. c) The complexes prepared from **1** and **2** showed the same spectral data. d) The complexes prepared from **3** and **4** showed the same spectral data. e) In H_2O. f) In acetone.

ucts were obtained. The molar conductivities of **5** and **6** are slightly lower than that usually found for 1 : 1 electrolyte probably due to the ion pair formation (Table 3).

Discussion

The experimental studies indicate the presence of complex cation (*trans*-$[Cr(NCS)_2(AA)_2]^+$) and anion ($[Cr(NCS)_4(AA)]^-$) in the double complexes which were synthesized pyrolytically from *cis*- and *trans*-$[Cr(NCS)_2(AA)_2]SCN$ according to the following sequence of reactions:

(i) $[Cr(NCS)_2(AA)_2][Cr(NCS)_4(AA)]$ **5** or **6** $\xrightarrow[\text{Cl}^-\text{ form}]{\text{Dowex 1-X8}}$

$[Cr(NCS)_4(AA)]^-$
(retained in column)

$[Cr(NCS)_2(AA)_2]^+ \xrightarrow{NH_4SCN}$ *trans*-$[Cr(NCS)_2(AA)_2]SCN$
(orange effluent) orange crystal

(ii) $[Cr(NCS)_2(AA)_2][Cr(NCS)_4(AA)]$ **5** or **6** $\xrightarrow[\text{Na}^+\text{ form}]{\text{Amberlite IR-120B}}$

$[Cr(NCS)_2(AA)_2]^+$
(retained in column)

$[Cr(NCS)_4(AA)]^- \xrightarrow{Et_4NBr} [Et_4N][Cr(NCS)_4(AA)]$
(red-violet effluent) red-violet crystal

The interesting feature of these thermal reactions are that the double complexes formed after the deamination of both *cis*- and *trans*-$[Cr(NCS)_2(AA)_2]SCN$ contain *trans*-$[Cr(NCS)_2(AA)_2]^+$ cation. Therefore during the deamination of the cis-complexes, cis-to-trans isomerization occured. In the course of our earlier studies,[4,8,9] we observed trans-to-cis isomerization in the bis(diamine)dihalogeno complexes containing diamine which is capable of forming five-membered chelate ring with chromium(III) ion, whereas cis-to-trans isomerization was found in the complexes containing six-membered diamine chelate ring. However, in this study, only cis-to-trans isomerization is observed irrespective of the ring size of the diamines. From this and previous results,[4,5] we tentatively assume that the anion size also plays a substantial role on the direction of the isomerization. The details are now under investigation.

It is interesting to note that only endothermic DSC peaks are observed for the deamination of trans-complexes (Fig. 2), whereas both endo- and exothermic peaks appeared in case of the cis-complexes. The exothermic peaks appeared during deamination of the cis-complexes is probably responsible for the isomerization because the isomerization of the *cis*-(diamine)-chromium(III) has been found to proceed exothermically.[5]

By utilizing these thermal reactions, the anionic

Table 3. R_f Values Obtained by Thin Layer Chromatography[a] and Molar Conductivities[b] (Λ) of the Complexes

Complex	R_f Value	$\Lambda/\Omega^{-1}\,cm^2\,mol^{-1}$
$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$[c]	0.816	71.0
$[Cr(NCS)_2(en)_2][Cr(NCS)_4(en)]$[d]	0.815	70.4
$[Cr(NCS)_2(tn)_2][Cr(NCS)_4(tn)]$[e]	0.846	70.5
$[Cr(NCS)_2(tn)_2][Cr(NCS)_4(tn)]$[f]	0.850	69.3

a) Acetone was used as eluents. A single plate was employed in each run. b) In acetone. c) Synthesized from *trans*-$[Cr(NCS)_2(en)_2]SCN$. d) Synthesized from *cis*-$[Cr(NCS)_2(en)_2]SCN$. e) Synthesized from *trans*-$[Cr(NCS)_2(tn)_2]SCN$. f) Synthesized from *cis*-$[Cr(NCS)_2(tn)_2]SCN$.

complex $[Cr(NCS)_4(AA)]^-$ can be prepared easily, which has previously been obtained with difficulty from solution reactions.[10] In addition the anionic complex $[Et_4N][Cr(NCS)_4(tn)]$ is newly prepared in the present study. Contrary to the earlier report,[10] we found a little low molar absorptivity (for the transition $^4A_{2g}\rightarrow{}^4T_{2g}$) for the complex $[Et_4N][Cr(NCS)_4(en)]$ in acetone[11] (Table 2).

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11) Reference 10 reported absorption bands at 515 ($\varepsilon_{max}=177\ mol^{-1}\,dm^3\,cm^{-1}$) and 392 nm ($\varepsilon_{max}=104\ mol^{-1}\,dm^3\,cm^{-1}$) for the complex $Na[Cr(NCS)_4(en)]$ in $10^{-2}\ mol\,dm^{-3}$ $HClO_4$.