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THE SOLID STATE REACTION BETWEEN HEXAAMMINECHROMIUM(III) COMPLEXES AND L-α-ALANINE

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ABSTRACT

The solid state reaction between $[Cr(NH_3)_6]X_3$ ($X^- = Cl$, I, SCN and NO_3) and L-α-alanine was studied under continuous rise in temperature and isothermal heating. Under continuous rise in temperature, the main products were $[Cr(NCS)_3(NH_3)_3]$ ($X^- =$ NCS) and $[Cr(L\text{-}ala)_3]$ ($X^- = NO_3$), when $[Cr(NH_3)_6]Cl_3$ and $[Cr(NH_3)_6]I_3$ as starting complexes were used; in both cases only the decomposition proceeds. Under isothermal heating at 150°C the main products were $[CrCl(NH_3)_5]Cl_2$ ($X^- =$ Cl), $[Cr(NH_3)_6]I_2$ ($X^- =$ I), $[Cr(NCS)_3(NH_3)_3]$ ($X^- =$ SCN) and $[Cr(L\text{-}ala)_3]$ ($X^- = NO_3$). In those matrix reactions, the ease of anion coordination was: $SCN^- > Cl^- > I^- >$ alanine. For the synthesis of tris(alaninato)chromium(III) complex the most desirable starting complex was $[Cr(NH_3)_6](NO_3)_3$.

The solid state reaction between $[Cr(en)_3]X_3$ type complexes and NH_4X ($X^- =$ F, Cl, Br, I and SCN), KX ($X^- =$ Cl, Br and I), and NaSCN have been reported by Wendlandt and Stembridge[1]. They reported that the reaction product, in most cases, was *cis*-$[Cr(en)_2Y_2]X$, where Y and X are the same or different anions, depending upon the matrix material employed and the thermal matrix method appears to be a useful new route for the synthesis of bis(ethylendiamine(chromium(III) complexes.

In the previous paper[2], the solid state reaction between $[Cr(NH_3)_6](NO_3)_3$ and L-amino acids has been utilized in the preparation of tris(amino acidato)chromium(III) complexes. The preparation of $[Cr(L\text{-}ala)_3]$ by the solid state reaction between $[Cr(NH_3)_6](NO_3)_3$ and L-alanine have been reported. No studies on the effect of the counter-ion have been reported.

In this paper, various hexaamminechromium(III) complexes, $[Cr(NH_3)_6]X_3$ ($X^- =$ Cl, I, SCN and NO_3), were heated with L-α-alanine under continuous rise in temperature and under isothermal heating at 150°C for studies on the ease of anion coordination. It will be seen that the anion which replaces the ammonia in the hexaamminechromium(III) complex comes from either the alanine or counter-ion.

EXPERIMENTAL

Preparation of complexes

Hexaamminechromium(III) chloride, iodide, thiocyanate and nitrate, $[Cr(NH_3)_6]X_3$ ($X^- = Cl$, I, SCN and NO_3), were prepared by the usual method described in the literature[3].

$[Cr(NH_3)_6]X_3$ (0.001 M) and L-alanine (0.003 M) were mixed in a mortar in order to make the solid state reaction proceed.

Continuous rise in temperature measurement

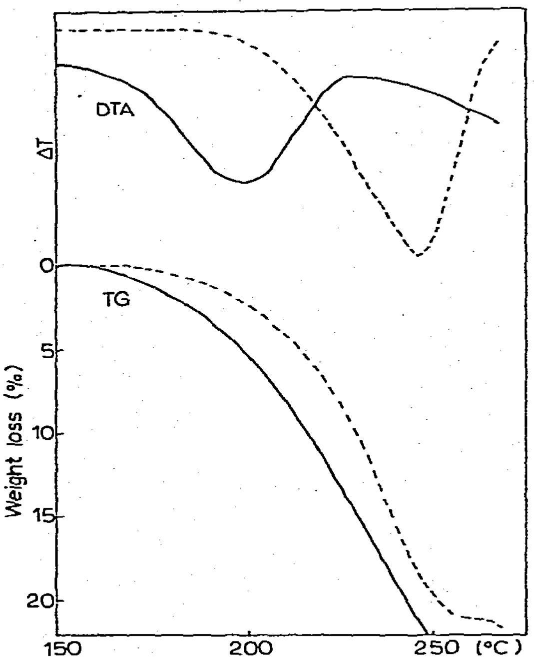
The rise in temperature measurement was carried out with a Metrimpex Derivatograph type OD-102. Derivatographic measurement was made in a nitrogen stream at a heating rate of 1 °C min^{-1}, 500 mg of the sample being used.

Isothermal measurement

Isothermal measurement was carried out in a Toyoroshi electric oven, the temperature of the sample being controlled at 150 ± 1 °C.

Apparatus

The IR spectra were measured in a KBr disc with a Hitachi EPI-G3 IR spectrophotometer.



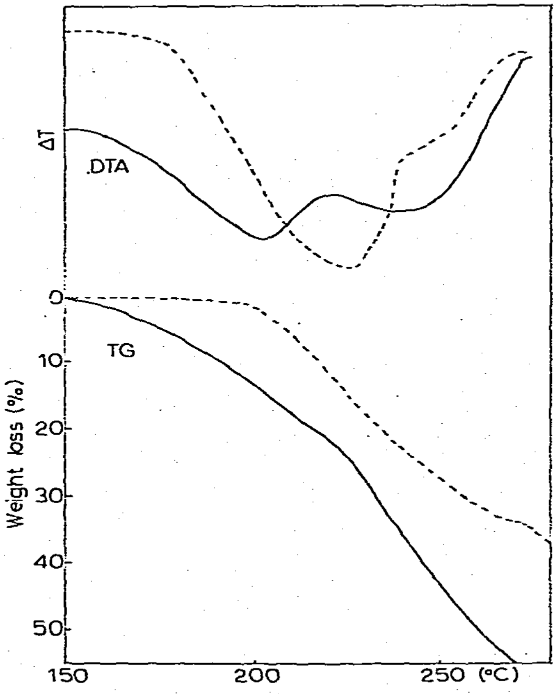


Fig. 1. The derivatograms of $[Cr(NH_3)_6]Cl_3$ (----) and the mixture of $[Cr(NH_3)_6]Cl_3$ and L-alanine (——).

Fig. 2. The derivatograms of $[Cr(NH_3)_6]I_3$ (----) and the mixture of $[Cr(NH_3)_6]I_3$ and L-alanine (——).

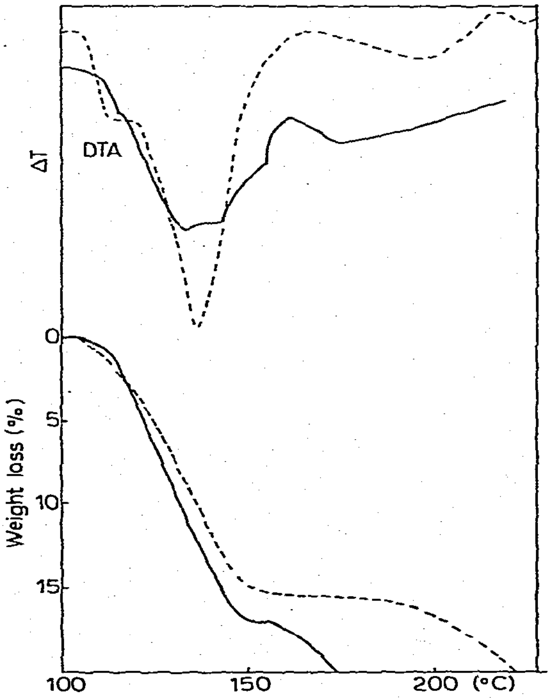
RESULTS AND DISCUSSION

Thermal reaction of hexaamminechromium(III) complexes with L-α-alanine under continuous rise in temperature

The derivatograms of $[Cr(NH_3)_6]Cl_3$ and the mixture of $[Cr(NH_3)_6]Cl_3$ and L-alanine are shown in Fig. 1. The TG and DTA curves of $[Cr(NH_3)_6]Cl_3$ show a weight loss in one step and a single endothermic peak, respectively.

The weight loss up to 250°C corresponds to liberation of three moles of ammonia, resulting in the formation of $[CrCl_3(NH_3)_3]$, while, the TG curve of the mixture show no distinct plateaus. The result suggests that only the decomposition proceeds, without the formation of $[CrCl_3(NH_3)_3]$ or $[Cr(ala)_3]$. The peak temperature of the endothermic peak appearing in the DTA curve of the mixture is different from that of pure $[Cr(NH_3)_6]Cl_3$. The reaction corresponding to this endothermic peak is not clear in the present work.

The derivatograms of hexaamminechromium(III) iodide and the mixture of that and L-alanine are given in Fig. 2. The TG curves of $[Cr(NH_3)_6]I_3$ and the mixture show no distinct plateau. Therefore, only the decomposition proceeds in both cases. Wendlandt and Chou^4 reported that the thermal decomposition of $[Cr(NH_3)_6]I_3$ has no tendency to give $[CrI_3(NH_3)_3]$ and the final product is Cr_2O_3.



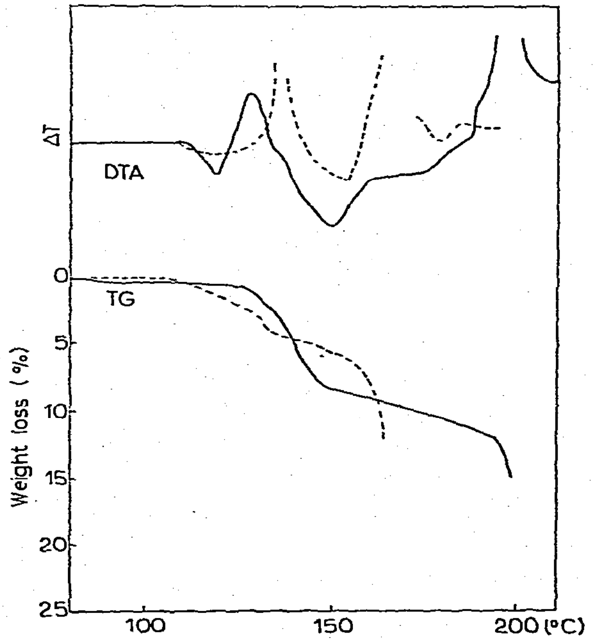


Fig. 3. The derivatograms of $[Cr(NH_3)_6](SCN)_3$ (----) and the mixture of $[Cr(NH_3)_6](SCN)_3$ and L-alanine (——).

Fig. 4. The derivatograms of $[Cr(NH_3)_6](NO_3)_3$ (----) and the mixture of $[Cr(NH_3)_6](NO_3)_3$ and L-alanine (——).

The derivatogram of the mixture of $[Cr(NH_3)_6](SCN)_3$ and L-alanine is given in Fig. 3, together with that of $[Cr(NH_3)_6](SCN)_3$ alone. The derivatograms of the mixtures are approximately similar to that of $[Cr(NH_3)_6](SCN)_3$ alone. The authour reported that the thermal product formed by liberating three moles of ammonia from $[Cr(NH_3)_6](SCN)_3$ is *cis–trans*-$[Cr(NCS)_3(NH_3)_3]$[5]. When the reaction product of the mixture up to 150 °C was washed with water, a reddish-purple substance was obtained. The IR spectrum of this substance is in complete agreement with *cis–trans*-$[Cr(NCS)_3(NH_3)_3]$.

The derivatograms of hexaamminechromium(III) nitrate and the mixture of that and L-alanine are shown in Fig. 4. The DTA curve of $[Cr(NH_3)_6](NO_3)_3$ shows an exothermic peak at 140 °C and burns at 170 °C, giving the second exothermic peak. The TG curve of the mixture gives a rapid weight loss at 130–150 °C and a slow one 150–190 °C; the former corresponds to liberation of 8–9 % of ammonia and the latter to 4–5 %. The DTA curve of the mixture gives three endothermic and one exothermic peaks. The first endothermic peak corresponds to melting of the mixture; the second and third endothermic peaks correspond to the liberation of ammonia. However, the reaction corresponding to the exothermic peak at 130 °C is not clear in the present work. The reaction product at 170 °C was dissolved in water. After filtration, the residue was $[Cr(ala)_3]$. $[Cr(ala)_3]$ was also obtained from the filtrate.

Thermal reaction of the mixture of hexaamminechromium(III) complexes and L-alanine under isothermal heating at 150 °C

Tanaka and Nagase[6] only obtained $[CrCl(NH_3)_5]Cl_2$ as product by isothermal heating of $[Cr(NH_3)_6]Cl_3$ at 150 °C. The reaction product of the mixture of $[Cr(NH_3)_6]Cl_3$ and L-alanine was dissolved in water (reaction time 90 min). The solution was kept standing overnight in a refrigerator. $[CrCl(NH_3)_5]Cl_2$ was deposited as red crystals.

The thermal reaction of $[Cr(NH_3)_6]I_3$ gave a green substance. Ephraim and Millmann[7] reported that $[Cr(NH_3)_6]I_3$ was reduced to $[Cr(NH_3)_6]I_2$ and $[Cr(NH_3)_6]I_3$ was recovered after cooling to room temperature. The green substance obtained was kept standing at room temperature for about 1 h to recover $[Cr(NH_3)_6]I_3$; therefore, the green substance was $[Cr(NH_3)_6]I_2$. After heating for 90 min, the colour of the mixture also changed to green. The green product was dissolved in methanol and in water; the filtrate was left standing at room temperature for a long time, the mixture of oily substance and $[Cr(NH_3)_6]I_3$ being recovered. The residue obtained by the filtration was the green substance, $[Cr(NH_3)_6]I_2$.

Oki et al.[5] reported that the isothermal heating of $[Cr(NH_3)_6](SCN)_3$ gives *trans*-$[Cr(NCS)_2(NH_3)_4]SCN$ and finally *cis–trans*-$[Cr(NCS)_3(NH_3)_3]$ at 140 °C. When the reaction temperature and reaction time were 150 °C and 30 min, the main product obtained from the mixture was also *cis–trans*-$[Cr(NCS)_3[NH_3)_3]$.

The fact that the thermal reaction of the mixture of $[Cr(NH_3)_6](NO_3)_3$ and L-alanine gives $[Cr(ala)_3]$ was reported by Oki[2].

The results obtained above are collected in Table 1. Wendlandt and Stembridge[1]

TABLE 1

THE RESULTS OF HEATING $[Cr(NH_3)_6]X_3$ IN A MATRIX OF L-ALANINE

X	*Product formed*	
	Continuous-rising reaction	*Isothermal reaction*
Cl^-	Decomposition	$[CrCl(NH_3)_5]Cl_2$
I^-	Decomposition	$[Cr(NH_3)_6]I_2$
SCN^-	$[Cr(NCS)_3(NH_3)_3]$	$[Cr(NCS)_3(NH_3)_3]$
NO_3^-	[Cr(L-ala)$_3$]	[Cr(L-ala)$_3$]

reported that the order of ease of coordination of anion(Y) was $F^- > SCN^- > Cl^- > Br^-$, in a "thermal matrix" reaction of $[Cr(en)_3]X_3$ type complex and NH_4Y, and the most desirable starting compound is $[Cr(en)_3]I_3$ for the synthesis of $[CrY_2(en)_2]Y$. In the solid state reaction between $[Cr(NH_3)_6]X_3$ and L-alanine, the most desirable starting complex is $[Cr(NH_3)_6](NO_3)_3$ for the synthesis of $[Cr(ala)_3]$. When the thiocyanate or chloride salt is used as starting complex, the ammonium of $[Cr(NH_3)_6]X_3$ is replaced by the counter-ion and $[Cr(ala)_3]$ was not obtained. In the case of the iodide salt, $[Cr(NH_3)_6]I_3$ was reduced only to $[Cr(NH_3)_6]I_2$. Therefore, the order of ease of anion coordination was: $NCS^- > Cl^- > I^- >$ ala, in the present work. The difference in the reaction products obtained under continuous rise in temperature and under isothermal heating was not observed, except for $[Cr(NH_3)_6]Cl_3$ and $[Cr(NH_3)_6]I_3$.

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