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Thermal isomerization of *cis*-[CrCl$_2$([15]aneN$_4$)]SCN in the solid state

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Abstract

The solid state thermal isomerization of *cis*-[CrCl$_2$([15]aneN$_4$)]SCN, where [15]aneN$_4$ is 1,4,8,12-tetraazacyclopentadecane, was investigated by means of TG and DTA methods. The complex was found to isomerize exothermically to the corresponding trans form via the formation of *cis*-[CrCl(NCS)([15]aneN$_4$)]Cl.

INTRODUCTION

We have already reported that coordinated ligands in metal complexes are unexpectedly movable even in the solid state; for example, the tris(diamine) complexes [Cr(aa)(bb)(cc)]X$_3$ easily evolve the diamine (aa) with the lowest boiling point, to form either *cis*- or *trans*-bis(diamine) complexes [CrX$_2$(bb)(cc)]X, depending on the anion size (X$^-$), where aa, bb and cc are the same or different diamines selected from 1,2-diaminoethane (en), 1,2-diaminopropane (pn) and 1,3-diaminopropane (tn) [1]. In addition, the coordinated ligands (X$^-$, bb and cc) in the bis(diamine) complexes are easily moved to undergo cis ↔ trans isomerization [2]. Our previous paper pointed out that even the macrocyclic complex *cis*-[CrCl$_2$([15]aneN$_4$)]Cl isomerizes thermally to the corresponding transform in the solid state, where [15]aneN$_4$ is 1,4,8,12-tetraazacyclopentadecane [3]. The occurrence of the isomerization is very interesting because [15]aneN$_4$ has a rigid structure obtained by fusing together 1,2-diaminoethane and three 1,3-diaminopropanes, as shown in Fig. 1. For the isomerization, we tentatively speculated that one of the four nitrogen atoms of [15]aneN$_4$ in the complex migrates to the coordination site of one of the coordinated chloride ions (Cl$^-$); the resulting vacant site is then occupied by the outer-sphere chloride ion (Cl^{-*}) to give a transient state [CrClCl*([15]aneN$_4$)]Cl; and

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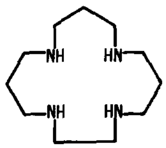

Fig. 1. 1,4,8,12-Tetraazacyclopentadecane ([15]aneN_4). For simplification, all methylene groups ($-CH_2-$) are omitted.

the original cis complex finally isomerizes to the trans form as below [3]

$$\textit{cis}\text{-}[CrCl_2([15]aneN_4)]Cl^* \rightarrow [CrClCl^*([15]aneN_4)]Cl$$
$$\rightarrow \textit{trans}\text{-}[CrCl_2([15]aneN_4)]Cl^*$$

The work reported here was undertaken to investigate the thermal isomerization of *cis*-$[CrCl_2([15]aneN_4)]SCN$ in the solid state in order to confirm this tentative speculation.

EXPERIMENTAL

1,4,8,12-Tetraazacyclopentadecane ([15]aneN_4) was prepared according to the known method [4]. The *cis*- and *trans*-$[CrCl_2([15]aneN_4)]Cl$ were prepared as reported previously [3].

cis-[CrCl$_2$([15]aneN$_4$)]SCN

This was obtained by the metathesis of *cis*-$[CrCl_2([15]aneN_4)]Cl$ with NaSCN in methanol. Found: C, 36.32; H, 6.41; N, 18.14%; Calcd. for $C_{12}H_{26}N_5SCl_2Cr$: C, 36.46; H, 6.63; N, 17.71%.

cis-[CrCl(NCS)([15]aneN$_4$)]Cl · 0.75 H$_2$O

As reported previously [3], *cis*-$[CrCl_2([15]aneN_4)]SCN$ was heated in the solid state at 170 °C for 70 h during which time the complex changed in color from purple to red. The red product thus obtained was dissolved in a minimum amount of methanol. The solution was passed through an alumina column and the adsorbed band was eluted with methanol. Green and then pink fractions were obtained which, using electronic spectrophotometry, were found to be *trans*-$[CrCl_2([15]aneN_4)]^+$ and *cis*-$[CrCl(NCS)([15]aneN_4)]^+$, respectively, as mentioned in the Results and Discussion section below. Then, the second pink fraction was gradually concentrated by roto-evaporation to give crystalline products. The products were collected by filtration, washed with acetone and air-dried. Recrystallization was carried out from methanol. Found: C, 35.05; H, 6.56; N, 17.02%; calcd. for $C_{12}H_{26}N_5SCl_2Cr \cdot 0.75\ H_2O$: C, 35.25; H, 6.78; N, 17.13%.

Measurements

TG and DTA measurements were carried out with a Seiko TA Station SSC 5000 system under a nitrogen stream (100 cm^3 min^{-1}), the sample weights being in the range 10–20 mg. The heating rate was 3.0 ° C min^{-1}. The heating process was also observed using a Chyo 100-L thermobalance. IR spectra were measured by a KBr disk method using a Jasco Model A-3 infrared spectrophotometer. Visible and ultraviolet electronic spectra were measured in 0.1 M HCl, 0.1 M $HClO_4$, water, methanol or acetone with a Jasco UVIDEC-505 UV/VIS recording digital spectrophotometer.

RESULTS AND DISCUSSION

Figure 2 shows the TG and DTA curves of *cis*-$[CrCl_2([15]aneN_4)]SCN$ and *cis*-$[CrCl(NCS)([15]aneN_4)]Cl \cdot 0.75H_2O$. The TG curve of *cis*-$[CrCl_2([15]aneN_4)]SCN$ remains almost unchanged up to about 280 ° C, above which the complex begins to decompose. Two small but distinct exothermic peaks appear at about 200 and 250 ° C in the DTA curve. The original purple color of the complex turned red at the first DTA peak (200 ° C), and then green at the second DTA peak (250 ° C).

For characterization of the first red products obtained, *cis*-$[CrCl_2([15]aneN_4)]SCN$ was heated isothermally at 170 ° C for several tens

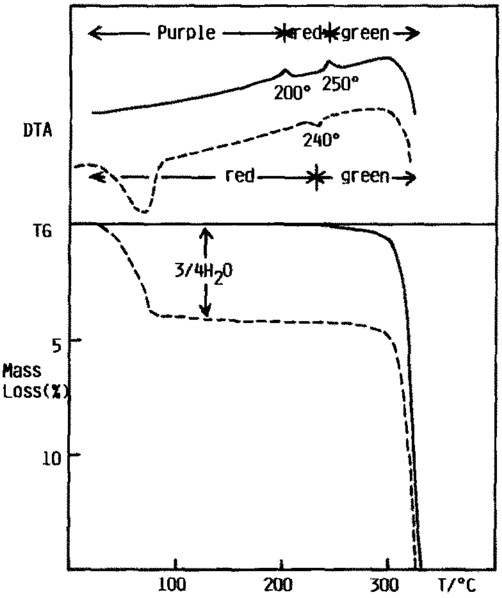

Fig. 2. TG and DTA curves of *cis*-$[CrCl_2([15]aneN_4)]SCN$ (———) and *cis*-$[CrCl(NCS)([15]aneN_4)]Cl \cdot 0.75\ H_2O$ (- - - - -).

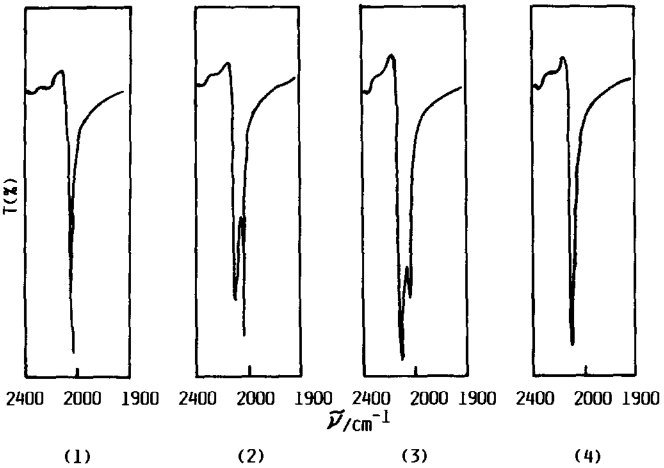

Fig. 3. IR spectra: 1, *cis*-[$CrCl_2$([15]aneN_4)]SCN; 2, the product obtained by heating the cis complex at 170 ° C for 10 h; 3, the product obtained by heating the cis complex at 170 ° C for 20 h; and 4, the product obtained by heating the cis complex at 170 ° C for 70 h.

of hours, and the reaction process was monitored by IR spectrophotometry (Fig. 3). As seen from the figure, the original complex *cis*-[$CrCl_2$([15]aneN_4)]SCN shows a single peak at 2030 cm^{-1} due to the CN-stretching vibration of free SCN^- [5]. However, the product obtained by heating the original complex for 10 h gives a new peak at 2080 cm^{-1} along with the original peak (2030 cm^{-1}). The appearance of the new peak is due to the CN-stretching vibration of coordinated NCS^-. In the IR spectrum of the product obtained after heating for 20 h, the intensity of the peak at 2030 cm^{-1} decreases as that at 2080 cm^{-1} increases. After 70 h, the peak at 2030 cm^{-1} completely disappears and only the peak at 2080 cm^{-1} is observed. The spectral changes indicate that the SCN^- ion in the original *cis*-[$CrCl_2$([15]aneN_4)]SCN complex is coordinated to chromium(III) ion during heating.

The red products obtained by heating *cis*-[$CrCl_2$([15]aneN_4)]SCN at 170 ° C for 70 h were then dissolved in methanol, and the solution was treated by column chromatography on alumina. The adsorbed band was then eluted by methanol to give two fractions: the first fraction was green and the second, pink. Rotary-evaporation of these two fraction yielded green and pink compounds, respectively. The electronic spectrum of the green compound gave three band maxima due to d–d transition: 17100 cm^{-1} ($\epsilon = 28.4$ mol^{-1} dm^3 cm^{-1}), 21000 ($\epsilon = 59.5$) and 24600 ($\epsilon = 78.8$); this spectrum is quite close to that of *trans*-[$CrCl_2$([15]aneN_4)]$^+$ [3]. The electronic spectrum of the pink compound gave two band maxima due to d–d transition: 19000 cm^{-1} ($\epsilon = 84.0$ mol^{-1} dm^3 cm^{-1}) and 24800 ($\epsilon =$ 81.9), which is essentially the same spectrum as that of *cis*-[$CrCl_2$([15]aneN_4)]Cl: 18500 cm^{-1} ($\epsilon = 70.1$ mol^{-1} dm^3 cm^{-1}) and 24800

($\epsilon = 71.4$), except that the former two bands appear at higher wave numbers by 500 and 1,000 cm^{-1} than the latter two, and the charge transfer band from the coordinated NCS^- to chromium(III) ion in the pink compound is lower in wave number by 5000 cm^{-1} compared with that from coordinated Cl^- to chromium (III) ion in *cis*-$[CrCl_2([15]aneN_4)]Cl$. This may indicate that the difference in the wave numbers of the band positions between the pink compound and *cis*-$[CrCl_2([15]aneN_4)]Cl$ is simply due to the fact that NCS^- ion is in a higher position than Cl^- ion in the spectrochemical series, and that the pink compound is *cis*-$[CrCl(NCS)([15]aneN_4)]Cl$. Thus, it can be concluded that one of the chloro ligands in *cis*-$[CrCl_2([15]aneN_4)]SCN$ was replaced by NCS^- ion at 200 ° C with the retention of cis configuration to give *cis*-$[CrCl(NCS)([15]aneN_4)]Cl$. Then, the coordinated NCS^- ion was again replaced by chloride ion in the outer sphere at 250 ° C with isomerization to form *trans*-$[CrCl_2([15]aneN_4)]SCN$.

The TG curve of *cis*-$[CrCl(NCS)([15]aneN_4)]Cl \cdot 0.75\ H_2O$ isolated as described in the Experimental section, shows the loss of 0.75 mole of the lattice water at 30–70 ° C; it then remains unchanged until the complex decomposes at about 280 ° C. However, a tiny but clear endothermic DTA peak appears at 240 ° C, at which temperature the complex changed in color from red to green. The green compound was identified spectrophotometrically as *trans*-$[CrCl_2([15]aneN_4)]Cl$.

On the basis of the above results, it can be concluded that the thermal isomerization of *cis*-$[CrCl_2([15]aneN_4)]SCN$ proceeds via the formation of *cis*-$[CrCl(NCS)([15]aneN_4)]Cl$ and that even macrocyclic ligands in the complexes can easily move in the solid state.

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