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The Synthesis and Properties of *trans*-$[CrCl_2(NH_3)_4]Cl \cdot H_2O$

Kenzo NAGASE and Nobuyuki TANAKA*
Department of Chemistry, Tohoku University, Kawauchi, Sendai
**Department of Chemistry, Faculty of Science, Tohoku University Katahira, Sendai*
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A simple method for the synthesis of *trans*-dichlorotetraamminechromium(III) chloride monohydrate was developed, and the configuration of the complex obtained was confirmed by measurements of the infrared and visible absorption spectra. It was found that the *cis-trans* isomerization took place in the solid state upon the thermal treatment of the complex at 200°C. The enthalpy change for the reaction was calculated to be 1.2 $kcal \cdot mol^{-1}$ by an analysis of the DSC curve.

Recently, several reports concerning the syntheses and properties of a *trans* type of tetraamminechromium(III) complex have been presented. Glerup and Schaffer[1] have reported the synthesis of a number of *trans*-diacidotetraamminechromium(III) complexes by the reaction of difluorotetrapyridinechromium(III) iodide with liquid ammonia in an autoclave. Hoppenjans and his co-workers[2] also obtained these complexes by a method based on the acid cleavage of the complex ion, $[(NH_3)_5Cr(OH)Cr(NH_3)_4Cl]^{4+}$. They[3] also investigated the stoichiometry and kinetics of the aquation reaction of *trans*-$[CrCl_2(NH_3)_4]^+$ in an acid solution. Brown *et al.*[4] measured the infrared absorption spectra of *trans*-$[CrCl_2(NH_3)_4]ClO_4$ in the frequency region of 200—600 cm^{-1}.

These syntheses, however, are somewhat complicated, and only a few studies have been made of the properties of these complexes. In the present study, a simple method for the synthesis of *trans*-$[CrCl_2(NH_3)_4]Cl \cdot H_2O$ was developed, and the infrared (400—4000 cm^{-1}) and visible absorption spectra of the complex were measured. Moreover, the thermal reactions of the complex in the solid state were examined.

Experimental

Material. Three complexes, $[Cr(NH_3)_6]Cl_3$,[5] *cis*-$[CrCl(H_2O)(NH_3)_4]Cl_2$[6], and *trans*-$[CoCl_2(NH_3)_4]Cl \cdot H_2O$,[7]

1) J. Glerup and C. E. Schäffer, *Chem. Commun.*, **1968**, 38.
2) D. W. Hoppenjans, J. B. Hunt, and Sr. M. J. Dechant, *ibid.*, **1968**, 514.
3) D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *Inorg. Chem.*, **7**, 2506 (1968).
4) D. H. Brown, D. R. MacSween, and D. W. A. Sharp, *Inorg. Nucl. Chem. Lett.*, **5**, 991 (1969).
5) M. Mori, *Nippon Kagaku Zasshi*, **74**, 253 (1953).
6) M. Mori, *ibid.*, **74**, 255 (1953).
7) S. M. Jϕrgensen, *Z. Anorg. Chem.*, **14**, 415 (1897).

were prepared according to the literature, *cis*-$[CrCl_2(NH_3)_4]Cl$ was obtained by heating *cis*-$[CrCl(H_2O)(NH_3)_4]Cl_2$ at 120°C for 3 hr in a vacuum.

Measurements. A Hitachi EPI-2G infrared spectrophotometer was used for the measurement of the infrared absorption spectra. The electronic spectra in solutions were measured by means of a Hitachi EPS-3 spectrophotometer. The diffuse reflectance spectra in the solid state were measured by means of a Hitachi EPS-3 spectrophotometer equipped with a standard integrating sphere attachment. The thermogravimetric(TGA) and differential scanning calorimetric(DCS) curves were obtained with a Rigakudenki 2008 CS thermobalance equipped with a standard differential scanning calorimeter in a dynamic nitrogen atmosphere. A ten-milligram sample in an aluminum crucible was used in each measurement. The furnace-heating rate was about 5°C min^{-1}.

Synthesis of trans-$[CrCl_2(NH_3)_4]Cl\cdot H_2O$. The starting material $[Cr(NH_3)_6]Cl_3$ (5 g) in powder was heated at 230°C in air until the color was converted to green. The product was washed thoroughly with cold water until the washings was colorless. The residue was non-electrolyte, its formula was represented as $[CrCl_3(NH_3)_3]$ on the base of the analytical data.

To the fine powder of $[CrCl_3(NH_3)_3]$ (3 g) in a 100 m*l*-stoppered flask, a 20-m*l* portion of 28% ammonia water was added. The mixture was then maintained at about 25°C for 5 days. *trans*-$[CrCl_2(NH_3)_4]Cl\cdot H_2O$ was formed as green crystals, those crystals were filtered off and washed with a small amount of cold water and then with ethanol, and air dried (yield *ca.* 1.5 g).

The complex thus obtained was purified by recrystallization from water at about 20°C. The crude material was dissolved in a minimum amount of water and filtered off. The green filtrate, in a desiccator with concd. HCl, was kept over night in a refrigerator, the green crystals which thus appeared were filtered off, washed with ethanol, and air dried.

Analysis. Found: Cr, 21.5; H, 5.95; N, 22.81; Cl, 42.9; H_2O, 7.4%. Calcd. for $[CrCl_2(NH_3)_4]Cl\cdot H_2O$: Cr, 21.27; H, 5.77; N, 22.92; Cl, 43.49; H_2O, 7.36%. The water content was determined from the TGA curve.

Results and Discussion

The infrared spectra of the complex and its related complexes are shown in Fig. 1. The M–N stretching band, which provides direct information about the coordination bond, appears in a lower-frequency region. The complex obtained gives the corresponding band at 469 cm^{-1} as a single peak, *trans*-$[CoCl_2(NH_3)_4]Cl\cdot H_2O$ also gives a single peak at 501 cm^{-1}, whereas *cis*-$[CrCl_2(NH)_3]_4Cl$ gives three peaks, at 437, 462, and 475 cm^{-1}.

The electronic spectra of the complex and its analogue are shown in Fig. 2. In the region of the *d-d* transition, the spectrum of the complex has absorption maxima at 17000, 21100, and 25100 cm^{-1}, its pattern very similar to that of *trans*-$[CrCl_2(en)_2]^+$, the spectrum of which has been measured by Carner and Esparza.[8]

The analytical data and the infrared and visible absorption spectra confirm that the complex obtained in this study has a *trans*-configuration and that its formula may be represented as *trans*-$[CrCl_2(NH_3)_4]Cl\cdot H_2O$.

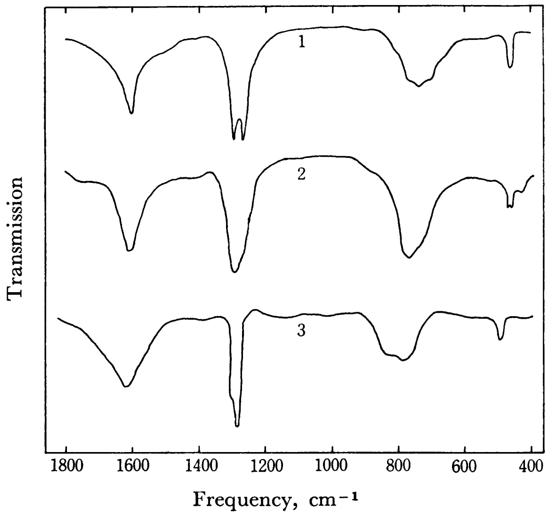

Fig. 1. Infrared spectra of (1) *trans*-$[CrCl_2(NH_3)_4]Cl\cdot H_2O$, (2) *cis*-$[CrCl_2(NH_3)_4]Cl$, and (3) *trans*-$[CoCl_2(NH_3)_4]Cl\cdot H_2O$.

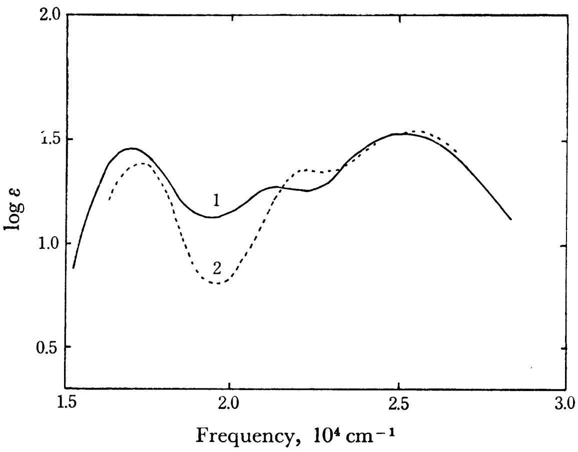

Fig. 2. Visible absorption spectra of (1) *trans*-$[CrCl_2(NH_3)_4]^+$ and (2) *trans*-$[CrCl_2(en)_2]^+$.

The TGA and DSC curves of *trans*-$[CrCl_2(NH_3)_4]Cl\cdot H_2O$ are shown in Fig. 3. From the TGA curve, it can be seen that the decomposition in the solid state takes place in three steps. The first step, which begins at 65°C and which is completed at 110°C (weight loss, 7.4%), is attributed to the evolution of one mole of hydrated water. The second one, which begins at 210°C and which is completed at 260°C (weight loss, 6.8%), is due to the evolution of one mole of ammonia. The nature of the third step, which begins at 260°C, is not yet clear.

On the DSC curve of *trans*-$[CrCl_2(NH_3)_4]Cl\cdot H_2O$, an endothermic peak for each weight loss was observed, but the peak for the second step splits into two. The shoulder peak may be due to the *cis-trans* isomerization.

In order to confirm the *cis-trans* isomerization, the diffuse reflectance spectra of the samples were measured before and after heating the complex. These spectra are shown in Fig. 4. The spectrum of the dehydrated complex which was obtained by heating

8) C. S. Carner and M. Esparza, *J. Inorg. Nucl. Chem.*, **29**, 2377 (1967).

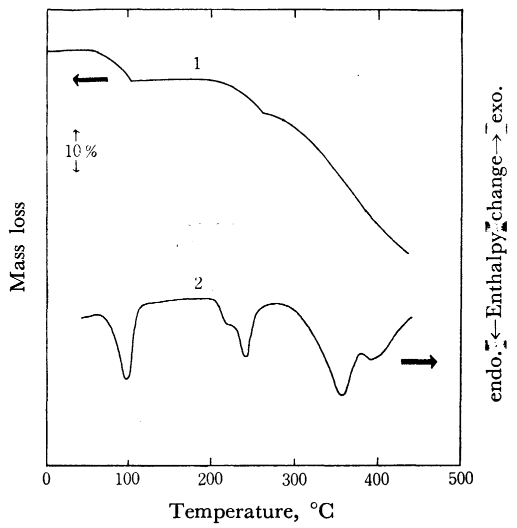

Fig. 3. TGA (1) and DSC (2) curves of *trans*-$[CrCl_2(NH_3)_4]Cl \cdot H_2O$ in a dynamic nitrogen atmosphere.

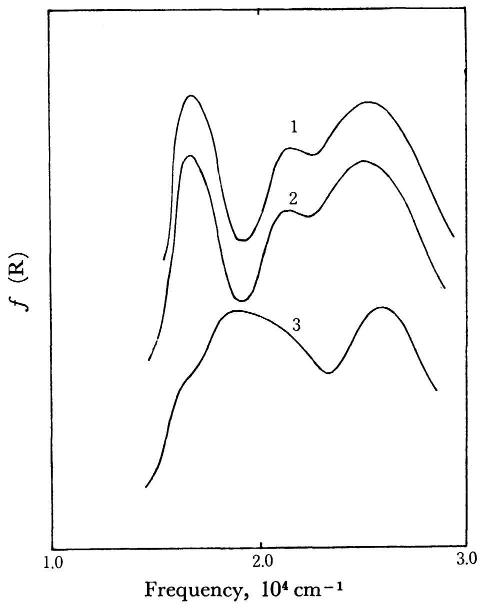

Fig. 4. Reflectance spectra of (1) *trans*-$[CrCl_2(NH_3)_4]Cl \cdot H_2O$, (2) *trans*-$[CrCl_2(NH_3)_4]Cl$, and (3) the sample obtained after heating *trans*-$[CrCl_2(NH_3)_4]Cl$ at 200°C for 24 hr in a sealed capillary tube.

trans-$[CrCl_2(NH_3)_4]Cl \cdot H_2O$ at 110°C for 3 hr in a vacuum is almost identical with that of the hydrated complex, from which it is clear that the *cis-trans* isomerization did not occur in the first step. When the dehydrated complex was heated at 220°C in a sealed capillary tube which was used for the purpose of suppressing the evolution of ammonia, the *cis-trans* isomerization occurred. The spectrum which is given by curve 3 in Fig. 4 suggests that the product was a mixture of the *cis* and *trans* isomers.

The enthalpy change, ΔH, for the isomerization reaction was calculated by means of an analysis of the DSC curve of *trans*-$[CrCl_2(NH_3)_4]Cl$. Since the isomerization was followed by the evolution of ammonia, as may be seen in Fig. 3, the peak area for the isomerization was estimated by drawing a curve which corresponded to the evolution of ammonia. The value of ΔH obtained for the isomerization (*trans*→*cis*) was 1.2 kcal·mol^{-1}. This value seems reasonable in view of the values reported in previous studies[9–11] for other isomerization reactions.

In order to confirm the existence of the reverse reaction, *cis*→*trans*, the *cis* isomer was heated under the same conditions as those employed for the *trans* isomer. The TGA and DSC curves of *cis*-$[CrCl(H_2O)(NH_3)_4]Cl_2$ are given in Fig. 5. From the TGA curves, it can be seen that the decomposition in the temperature

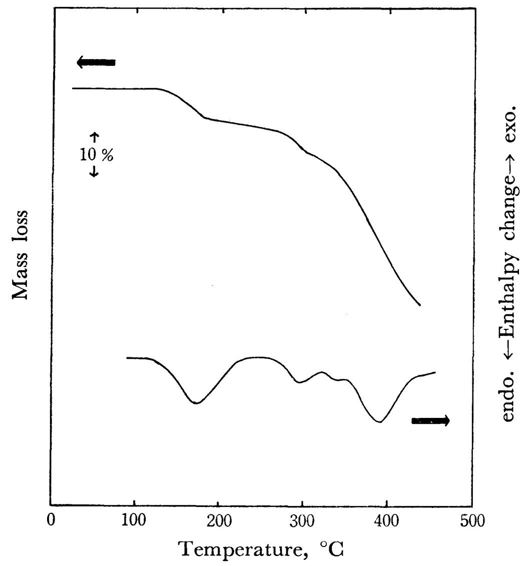

Fig. 5. TGA (1) and DSC (2) curves of *cis*-$[CrCl(H_2O)(NH_3)_4]Cl_2$ in a dynamic nitrogen atmosphere.

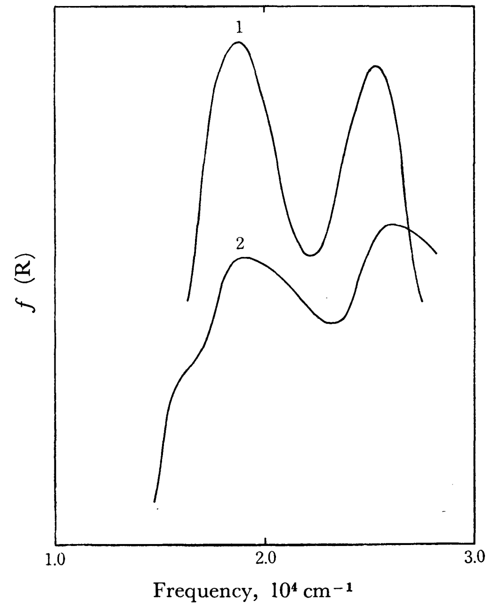

Fig. 6. Reflectance spectra of (1) *cis*-$[CrCl_2(NH_3)_4]Cl$ and (2) the sample obtained after heating *cis*-$[CrCl_2(NH_3)_4]Cl$ at 200°C for 24 hr in a sealed capillary tube.

9) R. Tsuchiya, K. Murai, A. Uehara, and E. Kyuno, This Bulletin, **43**, 1383 (1970).

10) Y. Kaji, A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 1906 (1970).

11) R. Tsuchiya, Y. Nakata, and E. Kyuno, *ibid.*, **44**, 705 (1971).

range from 25 to 500°C took place in three steps. In the temperature region from 142 to 200°C, the complex lost coordinated water to form *cis*-$[CrCl_2(NH_3)_4]$-Cl while at temperatures higher than 200°C the evolution of ammonia took place. Since the horizontal mass level was not observed between the evolution of water and the evolution of ammonia, pure *cis*-$[CrCl_2(NH_3)_4]Cl$ could not be obtained by heating *cis*-$[CrCl(H_2O)(NH_3)_4]Cl_2$ under the conditions employed for the measurement of the TGA curve. Therefore, the pure *cis*-$[CrCl_2(NH_3)_4]Cl$ used for the measurement was obtained by heating *cis*-$[CrCl(H_2O)(NH_3)_4]$-Cl at 120°C for 3 hr in a vacuum.

The *cis*-$[CrCl_2(NH_3)_4]Cl$ thus obtained was heated at 200°C for 24 hr in a sealed capillary tube. The reflectance spectrum of the product is given in Fig. 6, along with that of the *cis* isomer. The shoulder peak at 17000 cm^{-1} suggests that the products contained *trans* isomer. In fact, the *trans* isomer was separated from the product by the following procedure.

To the product (1 g) 20 m*l* of water was added, and then the mixture was filtered. The residue on a filter is a mixture of the *cis* isomer and a minute amount of $[CrCl_3(NH_3)_3]$ which was formed by the evolutoin of ammonia. The green filtrate was left over-night in a desiccator with concd. HCl, and then kept standing over night in a refrigerator. The green crystals formed were separated and washed with ethanol. The physical data of the product were identical with those of *trans*-$[CrCl_2(NH_3)_4]Cl\cdot H_2O$.

On the DSC curve, an endothermic peak for each mass loss was observed, but in the case of the *cis* isomer there was no peak corresponding to the *cis-trans* isomerization. From this result, it may be supposed that, when the *cis* isomer is heated in a dynamic nitrogen atmosphere the evolution of ammonia took place at a lower temperature than did the isomerization.

The equilibrium constant for the *cis-trans* isomerization reaction could not be obtained, since the side reaction, *cis*- or *trans*-$[CrCl_2(NH_3)_4]Cl \rightarrow [CrCl_3(NH_3)_3] + NH_3$, took place under the conditions employed in this study.

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