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The Thermal *trans*-to-*cis* Isomerization of $[CrCl_2(en)_2]Cl$ in the Solid Phase

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The *cis*↔*trans* isomerization reactions of transition metal complexes have been extensively studied in solution.[1] However, only a few studies have been recently reported on reactions in the solid phase,[2] and little is known about the mechanism of these solid-phase isomerizations. The thermal behavior of *trans*-$[CrCl_2(en)_2]Cl$ in the solid phase was studied by differential thermal analysis (DTA) and compared with that of the *cis*-isomer. *trans*-$[CrCl_2(en)_2]Cl$ showed an endothermic peak at 275°C and then an exothermic peak at 285°C, after which the sample turned reddish violet from gray green, accompanied by an appreciable bulk compression, and above 300°C it decomposed. On the contrary, the *cis*-form showed no peak up to 300°C, and above 300° it decomposed quite like the product obtained by heating *trans*-isomer up to 300°C. The *trans*-to-*cis* isomerization of $[CrCl_2(en)_2]Cl$ at 250—290°C was suggested and confirmed by measurements of the infrared and electronic spectra of the samples.

Experimental

Both *trans*-$[CrCl_2(en)_2]Cl$ and *cis*-$[CrCl_2(en)_2]Cl \cdot H_2O$ were prepared as has been described in the literature.[3] DTA studies were made using the Rigaku-Denki automatic recording DTA apparatus, in which the inert material was alumina, with a helium gas flow through the sample. A powdered sample of 100 mg sandwiched between alumina layers was used, and the heating rate was 5°C min^{-1}. The Rigaku-Denki differential scanning calorimeter (DSC) was also used for a more detailed inspection, with a 20-mg sample and a heating rate of 3°C min^{-1}. The infrared spectra were recorded as Nujol and hexachlorobutadiene mulls on a Model 601-F (4000—200 cm^{-1}) grating spectrophotometer of the Japan Spectro Co., Ltd. The electronic spectra of the samples in aqueous hydrochloric acid solutions were obtained on a Hitachi EPS-2U recording spectrophotometer.

Results and Discussion

The DTA curve obtained for the *trans*-$[CrCl_2(en)_2]Cl$ is given in Fig. 1, together with that of *cis*-$[CrCl_2(en)_2]Cl \cdot H_2O$. In the case of the former, an endothermic peak appears at 275°C and then an exothermic peak at 285°C, but in the case of the latter these peaks do not appear. Above 300°C both complexes decompose in almost the same way. In the heat treatment up to 300°C, the *trans*-complex shows only a slight weight loss (less than one percent), but in the above-peak region it changes in color to a dark-reddish violet from the initial gray green, and there is an accompanying appreciable bulk compression. This product, once obtained from the *trans*-form on being heated up to 300°C, shows no color change upon cooling and no peak in DTA curve when reheated to 300°C. To present the details of the thermal behavior of the *trans*-complex in the 230—300°C region, the DSC curve is shown in Fig. 2. It is noteworthy that small endothermic and exothermic peaks precede the principal peaks.

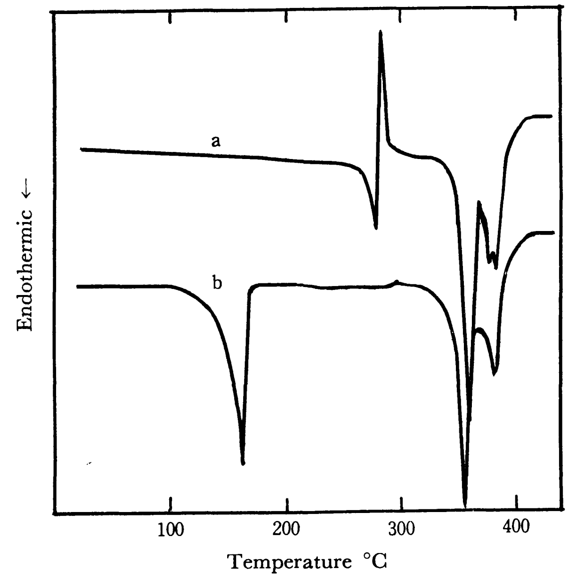

Fig. 1. The DTA curves of *trans*-$[CrCl_2(en)_2]Cl$ (a), and *cis*-$[CrCl_2(en)_2]Cl \cdot H_2O$ (b).

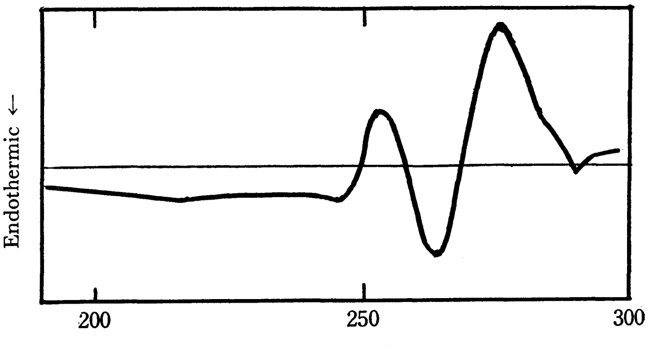

Fig. 2. The DSC curve of *trans*-$[CrCl_2(en)_2]Cl$.

These results suggest that *trans*-$[CrCl_2(en)_2]Cl$ may isomerize to the *cis*-form irreversibly on being heated in the temperature range of 250—290°C. This is confirmed by the results of the measurements

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd Ed., John Wiley & Sons, Inc., New York, N. Y. (1967), pp. 274—291.

[2] N. Tanaka and K. Nagase, This Bulletin, **42**, 2854 (1969); R. Tsuchiya, K. Murai, A. Uehara, and E. Kyuno, *ibid.*, **43**, 1383 (1970); Y. Kazi, A. Uehara, E. Kyuno, and R. Tsuchiya, *ibid.*, **43**, 1906 (1970); F. C. Chang and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **32**, 3535 (1970), *etc.*

[3] P. Pfeiffer, P. Koch, G. Lando, and A. Trieschmann, *Ber.*, **37**, 4255, 4269, 4277 (1904).

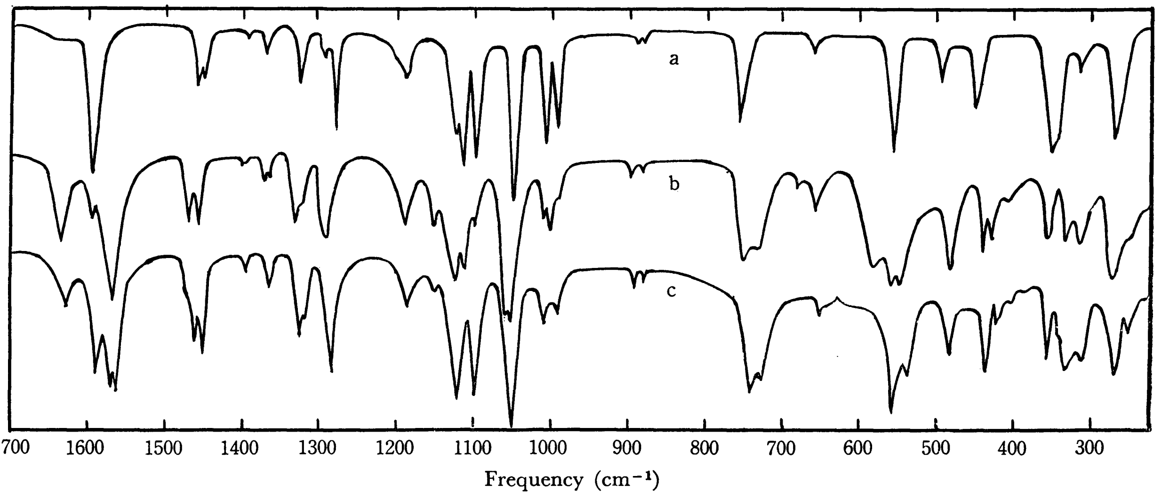

Fig. 3. Infrared spectra of *trans*-$[CrCl_2(en)_2]Cl$ (a), *cis*-$[CrCl_2(en)_2]Cl \cdot H_2O$ (b) and the product obtained from *trans*-form by heating up to 300°C (c).

of the electronic and infrared spectra. The resulting sample, when dissolved in an aqueous hydrochloric acid solution, exhibits absorption maxima at 528 mμ and 402 mμ, these values are in agreement with the values for the *cis*-form.[4] The point group of *trans*-$[CrCl_2(en)_2]^+$ is D_{2h}, on the contrary, that of the *cis*-form is C_2, and the infrared spectra differ appreciably in these two isomers.[5] This is ascertained in our measurements; the results are shown in Fig. 3, together with the results for the sample produced by heating the *trans*-complex up to 300°C. These results clearly indicate the *trans*-to-*cis* isomerization.

The above results suggest that, by the bond-breaking of a Cr-N linkage and the anation of Cl^-, *trans*-$[CrCl_2(en)_2]Cl$ may change first to *cis,trans*-$[CrCl_3(en)_2]$, in which one (en) behaves as an unidentate ligand, and may simultaneously melt and subsequently change to *cis*-$[CrCl_2(en)_2]Cl$ and resolidify. A similar type of *cis*↔*trans* isomerization, in which melting, isomerization and resolidification occur successively, has been reported in the case of *cis*-$[PtCl_4\{(C_2H_5)_2S\}_2]$, which isomerizes to the *trans*-form in the temperature range of 120—140°C.[6]

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[4] M. Esparza and C. S. Garner, *J. Inorg. Nucl. Chem.*, **29**, 2377 (1967).

[5] M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc.*, *A*, **1967**, 592.

[6] F. G. Angell, H. D. K. Drew, and W. Wardlaw, *J. Chem. Soc.* **1930**, 349; (*cf.* G. B. Kauffman, J. Hwa-san Tsai, and L. T. Takahashi, "Inorganic Syntheses," Vol. VIII, Ed. by H. F. Holtzlaw, Jr., McGraw-Hill, New York (1966) p. 247.