Thermal *trans-cis* Isomerization of $[CrBrH_2O(NH_3)_4]Br_2$

Yoriko KAJI, Akira UEHARA, Eishin KYUNO and Ryokichi TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

(Received March 10, 1970)

There are only a few examples of thermal *trans-cis* isomerization of transition metal complexes in solid phase.[1] In general, the isomerization of the complexes which contain crystalline or coordinated water occurs simultaneously with dehydration or after.[2] Isomerization prior to dehydration is still unknown. One of such rare examples was investigated in the present work.

When the complex, *trans*-$[CrBrH_2O(NH_3)_4]Br_2$,[3] was heated, it turned to reddish-violet from violettish-brown, and the coordinated water was then liberated. This suggests a change from *trans* to *cis* form. The derivatogram of the *trans* complex is given in Fig. 1. It shows an endothermic peak without any mass loss in the DTA curve at 145°C.

In order to confirm the *cis-trans* isomerization, absorption spectra of the compounds obtained after heating the complex with a thermobalance at both 143 and 153°C were measured by diffusion reflectance method in solid state. They are given in Fig. 2, together with those obtained at room temperature for the starting *trans* complex and for the *cis* isomer prepared by the standard method.[3]

The *d–d* band in the long wavelength region of the starting complex is split into two peaks, indicating the validity of the *trans* form. On heating, the splitting of these peaks became gradually weaker, approaching one peak corresponding to that of the *cis* form. The results suggest that *trans-cis* isomerization occurs in thermal reaction.

The enthalpy change, ΔH, for the reaction was calculated to be 1.9 kcal·mol^{-1} by analysis of DTA, and the activation energy, E^*, was evaluated by the same analysis to be 87 kcal·mol^{-1}. The values are very interesting for discussing the mechanism of isomerization reaction in the solid phase.

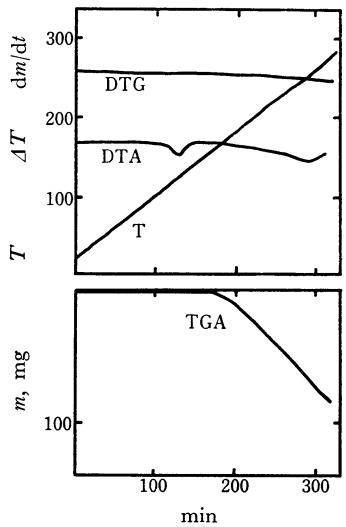

Fig. 1. Derivatogram for *trans*-$[CrBrH_2O(NH_3)_4]Br_2$.

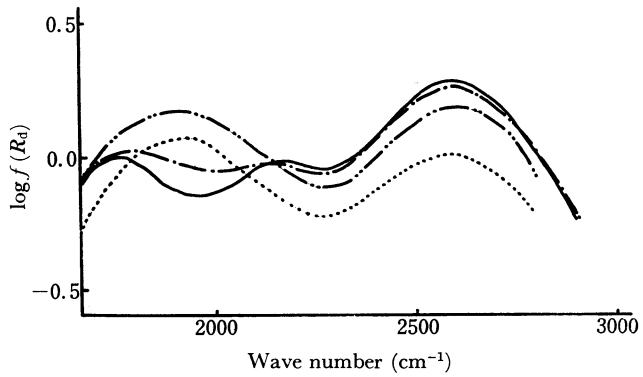

Fig. 2. Absorption spectra for *trans*-$[CrBrH_2O(NH_3)_4]Br_2$ (————), *cis*-$[CrBrH_2O(NH_3)_4]Br_2$ (·····), and the compounds obtained after heating at 143 (—·—·—) and 153°C (—··—··—).

1) H. E. LeMay, Jr., and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 5577 (1967).

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

3) D. W. Hoppenjans and J. B. Hunt, *Inorg. Chem.*, **8**, 505 (1969).