CHEMISTRY LETTERS, pp. 339-344, 1977. Published by the Chemical Society of Japan

EVIDENCE FOR A BOND RUPTURE MECHANISM IN TRANS-TO-CIS ISOMERIZATION OF $[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$ IN SOLID-PHASE

Ryokichi TSUCHIYA, Tadatsugu YOSHIKUNI, Shigeo NAKAGAWA,* Akira UEHARA, and Eishin KYUNO*

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

*Department of Pharmaceutical Science, School of Pharmacy, Hokuriku University, Kanazawa 920

The trans-to-cis isomerization of $[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$ (bn = d,ℓ-2,3-diaminobutane) was investigated in the solid-phase. A bond rupture mechanism was proposed for the isomerization from the fact that the trans-complex (green) is converted into cis-$[CrCl_2bn_2]Cl$ (violet) via the intermediate $[CrCl_3bn_2]$ (bluish violet) in which one of d,ℓ-2,3-diaminobutanes is coordinated as unidentate toward chromium(III) ion.

Since the age of Werner,1) much has been discussed on the mechanisms involved in the geometrical and optical isomerizations of octahedral tris- and bis-(bidentate ligand) metal complexes.2—6) Two main processes have been proposed on the mechanisms: one is intramolecular process (bond rupture and twisting mechanisms) and the other is intermolecular process (dissociative and displacement mechanisms). In the solid-phase, the subject has, however, been approached in a few papers and twisting mechanism was preferably accepted.7,8)

We have systematically examined the trans ⟷ cis isomerization of $[CrX_2(a\text{-}a)_2]X$ type complexes in the solid-phase, where X is a halide ion and a-a is a diamine, respectively.9—11) Especially we have been concerned with the effect of lattice waters, coordinated halide ions, diamines and outer-sphere ions on the isomerization. From the facts that the isomerization in the solid-phase needs no participation of lattice waters and the reaction is always accompanied by an uncertain sharp exothermic DTA peak in the chromium(III) complexes, we have tentatively speculated that a bond rupture mechanism may be preferentially involved in the isomerization. Unfortunately, details have remained insolvable.

Our previous speculation would be verified, if the fact were found that $[CrX_2(a\text{-}a)_2]X$ isomerizes via the formation of an intermediate $[CrX_3(a\text{-}a)_2]$ in which one of diamines functions as unidentate toward chromium(III) ion.

We have now found that the complex trans-$[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$ isomerizes to cis-isomer through the formation of the intermediate $[CrCl_3bn_2]$. The paper is therefore concerned with the trans-to-cis isomerization of $[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$ and the mechanism thereof in the solid-phase.

Preparation of trans-dichlorobis(d,ℓ-2,3-diaminobutane)chromium(III) Chloride Hydrochloride Dihydrate, trans-$[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$. trans-$[CrF_2bn_2]ClO_4$ was at first derived from trans-$[CrF_2(py)_4]ClO_4$[12)] according to the known method[12,13)] except that d,ℓ-2,3-diaminobutane was used in place of ethylenediamine. One gram of the difluoro bis(bn) complex was added to about 10 ml of concentrated hydrochloric acid and the mixture was reacted at ambient temperature in the dark with continuous stirring for about 12 hr. The product thus obtained was collected by filtration and then washed with concentrated hydrochloric acid and acetone, and air-dried. Yield about 0.6 g.

Purification was carried out as follows: the product was dissolved in 10 ml of 2 M hydrochloric acid and the solution was allowed to stand over concentrated sulfuric acid in a desiccator. About 50 ml of concentrated hydrochloric acid was also placed in the desiccator to saturate it with hydrogen chloride gas. After about 2 days, large rectangular dark-green crystals were obtained, which were collected by filtration, washed with concentrated hydrochloric acid, and air-dried. Yield about 0.3 g.

Found: C, 23.20; H, 7.13; N, 13.68 %. Calcd for $CrC_8H_{29}N_4O_2Cl_4$: C, 23.60; H, 7.18; N, 13.76 %.

Thermal Behavior of trans-$[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$ in the Solid-phase. The thermal behavior of the complex in the solid-phase was observed by means of derivatography in a nitrogen stream at the heating rate of 1°C min^{-1}. Three tenth grams of the sample was used in each run. The TG curve in Fig. 1 shows that the complex evolves one mole of hydrogen chloride at 55—80°C and then 2 moles of water at 100—140°C. The fact that the first evolution step corresponds to that of a hydrogen chloride was qualitatevely confirmed by the occurence of reaction of a silver nitrate solution. The color (green) of the complex was essentially unchanged at these steps. Then no change was found in the TG curve up to 200°C.

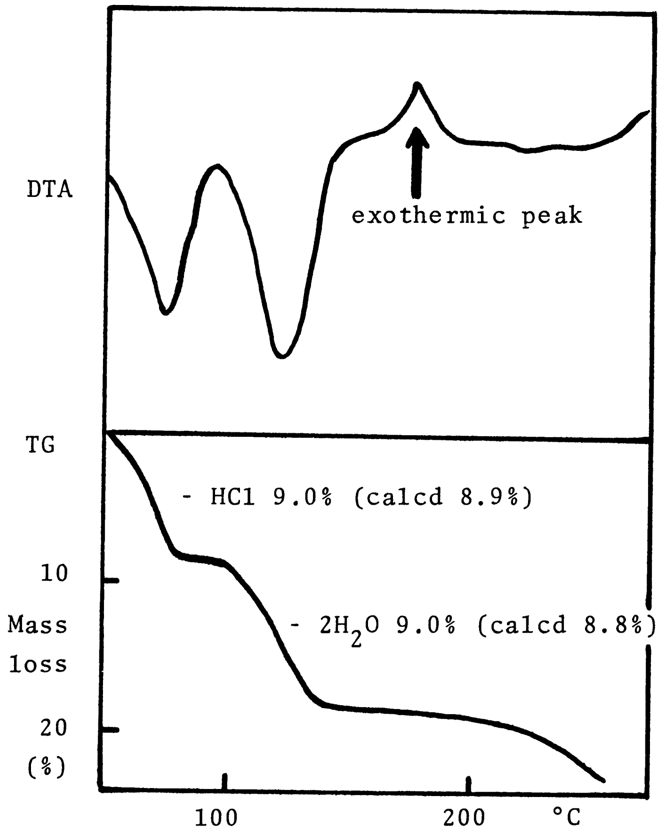


Fig. 1 Derivatogram of trans-$[CrCl_2bn_2]Cl \cdot HCl \cdot 2H_2O$.

Characteristically, a small but clear exothermic DTA peak appears at 180°C, and the complex changed in color to bluish violet from original green at this stage. The complex turned finally violet at 180—200°C, and then was complicately decomposed above 200°C. The bluish violet (hereinafter referred to as the intermediate) and the violet products were, as will be mentioned in the later sections, $[CrCl_3bn_2]$ and cis-$[CrCl_2bn_2]Cl$, respectively.

Isolation of the Intermediate. The intermediate which was formed at 180°C during the heating was sparingly soluble in water, but the starting material (trans-complex) and the final product (cis-complex) were readily soluble in water.

One and eight tenth grams of finely powdered trans-complex was spread in a thin layer on a watch glass and heated at 180°C for 10 min. The product thus obtained was washed throughly with water until washings became colorless, washed with acetone and ether, and air-dried. The crude product was dissolved in 40 ml of dimethylformamide, and thereto 35 ml of ether was added gradually for about 3 hr. The bluish crystals obtained were collected by filtration, washed with ether, and air-dried. Yield about 40 mg.

Found: C, 27.23; H, 7.41; N, 15.97 %. Calcd for $CrC_8H_{26}N_4OCl_3$: C, 27.22; H, 7.43; N, 15.89 %.

The lattice water in the crystals probably comes from trace amounts of water in ether or dimethylformamide employed in the procedure.

Electronic Spectra. Figure 2 shows the electronic spectra of the starting material (trans-$[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$), the intermediate isolated in the above section ($[CrCl_3bn_2]\cdot H_2O$), and cis-$[CrCl_2bn_2]Cl$ prepared according to the method described in literature.[14)]

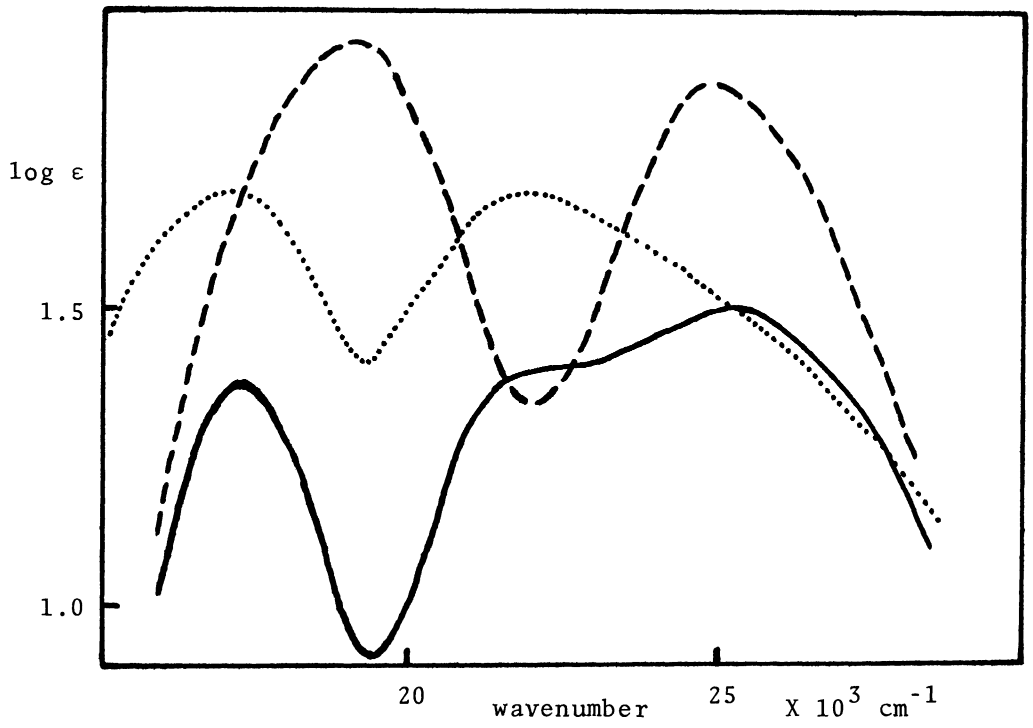


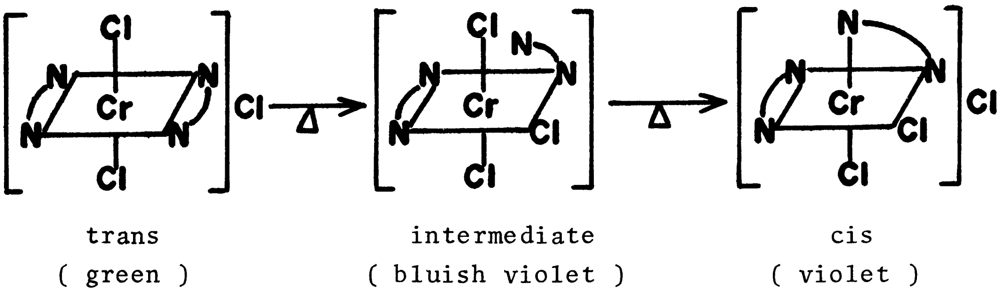
Fig. 2 Electronic spectra of trans-$[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$ (———) in 0.1 M $HClO_4$, the intermediate (·········) in DMF and cis-$[CrCl_2bn_2]Cl$ (— — —) in 0.1 M $HClO_4$.

As seen from the figure, trans-$[CrCl_2bn_2]Cl\cdot HCl\cdot 2H_2O$ has, as expected, three absorption bands in the range of d-d transition [17.2 X 10^3 cm^{-1}(log ε = 1.38), 22.2 X 10^3 cm^{-1}(log ε = 1.39) and 25.2 X 10^3 cm^{-1}(log ε = 1.50)] and cis-$[CrCl_2bn_2]Cl$ has two bands at 18.9 X 10^3 cm^{-1}(log ε = 1.90) and 24.9 X 10^3 cm^{-1} (log ε = 1.87). On the other hand, the intermediate has two bands at 17.0 X

10^3 cm^{-1}(log ε = 1.70) and 22.0 X 10^3 cm^{-1}(log ε = 1.70); the inspection of the spectrum reveals that appreciable shoulders are detectable at about 15.6 X 10^3 cm^{-1} and 24.5 X 10^3 cm^{-1}. The occurrence of these shoulders may, as the study on the [Cr and Co Cl_3dien] complexes has reported,16) suggest that three chloride ions in the intermediate are arranged in a mer position.

In addition, it must be mentioned that the spectra of the bluish violet and the violet products obtained in the heating process closely resemble those of the intermediate isolated in the above section and cis-[$CrCl_2bn_2$]Cl prepared as the reference material.

Reaction Scheme of the Isomerization. On the basis of the above results, the isomerization of trans-[$CrCl_2bn_2$]Cl·HCl·$2H_2O$ can be schematically represented as follows:



It may be concluded that the bond rupture of one of d,ℓ-2,3-diaminobutanes is operative in the reaction.15) It seems that the same mechanism is also true for other complexes of the type [$CrX_2(a\text{-}a)_2$]X which isomerize with analogous exothermic DTA peaks.

References

1) A. Werner, Ber., 45, 3061 (1912).

2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., John Wiley and Sons, Inc., 1967, p. 247.

3) N. Serpone and D. G. Bickley, Progress in Inorganic Chemistry, Vol. 17, J. O. Edwards ed., John Wiley and Sons, Inc., 1972, p. 391.

4) J. J. Fortman and R. E. Sievers, Coord. Chem. Rev., 6, 331 (1971).

5) K. Saito, Kagaku Sosetsu, No. 13, Chemical Society of Japan ed., Tokyo University Publisher, 1976, p. 178.

6) D. G. Bickley and N. Serpone, Inorg. Chem., 15, 2577 (1976).

7) C. D. Schmulbach, J. Brady, and F. Dachile, Inorg. Chem., 7, 287 (1968).

8) C. Kutal and J. C. Bailar, Jr., J. Phys. Chem., 76, 119 (1972).

9) R. Tsuchiya, T. Ohki, A. Uehara, and E. Kyuno, Thermochimica Acta, 12, 413 (1975).

10) R. Tsuchiya, H. Imai, A. Uehara, and E. Kyuno, Chem. Lett., 1976, 1159.

11) T. Yoshikuni, R. Tsuchiya, A. Uehara, and E. Kyuno, Bull. Chem. Soc. Jpn., 50, (1977), in press.

12) J. Glerup, J. Josephsen, K. Michelsen, E. Pedersen, and C. E. Schäffer, Acta Chem. Scand., 24, 247 (1970).

13) J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, Inorg. Chem., 7, 736 (1968).

14) C. P. Madhusudhan and J. A. McLean, Jr., Inorg. Chem., 14, 82 (1975).

15) The study on the isotopic exchange of cis- and trans-$[CoCl_2en_2]Cl^*$ shows that the Cl ion in inner-sphere is exchanged by the Cl^* ion in outer-sphere in the solid-phase. This is also indicative of the inclusion of a bond rupture process: see G. B. Schmidt and K. Rössler, Radiochim. Acta, 5, 123 (1966).

16) D. A. House, Inorg. Nucl. Chem. Lett., 3, 67 (1967).

(Received January 17, 1977)