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SOLID-PHASE THERMAL S_E REACTION OF $[Cr(NH_3)_6][Al(nta)_2]\cdot 4H_2O$*

Ryokichi TSUCHIYA, Akira UEHARA, and Eishin KYUNO

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

$[Cr(NH_3)_6][Al(nta)_2]\cdot 4H_2O$ was newly prepared, of which solid-phase thermal reaction was investigated by means of derivatography. The results showed that the complex converts finally into $Al[Cr(nta)_2]$. The reaction is unique in respect to both involvement of metal substitution and occurrence of variation in coordination types of the nitrilotriacetate ions.

Previously, we reported that metal substitution takes place in the solid-phase thermal reaction of Cr(III)-ammine——Al(III)-oxalato series of double complexes.1) In the case, the use of oxalate ions made it possible to find such an interesting phenomenon, since the ligand (oxalate ion) has, potentially, a possibility of behaving bilaterally toward both metal ions (chromium and aluminum ions). In the present report, nitrilotriacetate ion (nta) was selected in place of oxalate ion from the standpoint that thermal mobilities of atoms or molecules may appear much more easily than they were expected. Nitrilotriacetate ion resembles oxalate ion in the inclusion of $-COO^-$ in its entity; namely it is also capable of functioning as a bilateral ligand toward both metal ions.

Preparation of Complexes. 1) Potassium Bis(nitrilotriacetato)aluminate(III) Hexahydrate, $K_3[Al(nta)_2]\cdot 6H_2O$ (white). Nitrilotriacetic acid (38.2 g, 0.2 mole) was added to a suspension of freshly prepared aluminum hydroxide (7.8 g, 0.1 mole) in 500 ml of water. The mixture was allowed to boil until it was completely dissolved, and thereto a solution of potassium hydroxide (16.8 g, 0.3 mole) in 200 ml of water was dropwise added. The resulting solution was concentrated to about half of its volume and was allowed to stand overnight in a refrigerator. White powdery precipitates were obtained, which were purified by recrystallization from water.

Found: C, 23.1; H, 3.66; N, 4.66 %. Calcd for $K_3[Al(C_6H_6O_6N)_2]\cdot6H_2O$: C, 22.8; H, 3.82; N, 4.46 %.

2) Hexaamminechromium(III) Bis(nitrilotriacetato)aluminate(III) Tetrahydrate, $[Cr(NH_3)_6][Al(nta)_2]\cdot4H_2O$ (yellow). It is desirable that the starting materials for use in preparing the complex are purified beforehand. Three and four tenth grams (0.01 mole) of $[Cr(NH_3)_6](NO_3)_3$ and 5.2 g (0.01 mole) of $K_3[Al(nta)_2]\cdot6H_2O$ were dissolved separately in about 300 ml of water, and then they were mixed. The mixture was allowed to stand in a refrigerator for 2 days, from which yellow crystals were obtained. The product could not be recrystallized because it was sparingly soluble in water and any other optimum solvent could not be found, but analyses evidenced that it was highly pure as follows:

Found: C, 22.5; H, 6.10; N, 17.6 %. Calcd for $[Cr(NH_3)_6][Al(C_6H_6O_6N)_2]\cdot4H_2O$: C, 22.9; H, 6.05; N, 17.8 %.

Derivatographic Measurement.

The thermal reaction of $[Cr(NH_3)_6][Al(nta)_2]\cdot4H_2O$ in solid-phase was observed by means of derivatography at the heating rate of 1°C/min in a nitrogen stream. Four hundred milligrams of the complex was used. The TG curve in Fig. 1 indicates that the complex evolves 4 moles of water of crystallization at 40 to 100°C in two separate steps and then loses 6 moles of ammonia at 190 to 230°C, at which step the color of the complex changes to pink from original yellow.

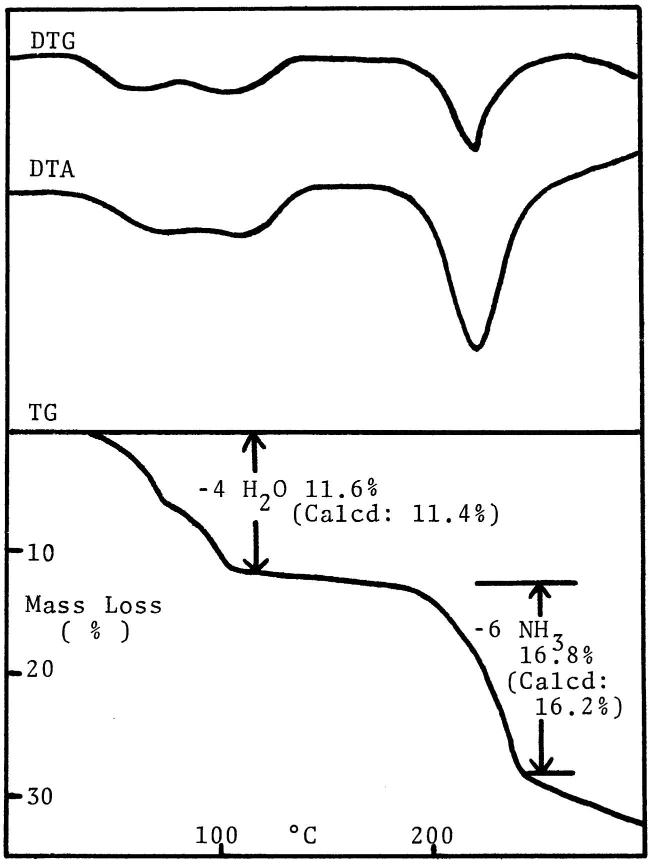

Fig. 1 Derivatogram of $[Cr(NH_3)_6][Al(nta)_2]\cdot4H_2O$.

IR Spectra. Figure 2 shows the IR spectra of $K_3[Al(nta)_2]\cdot6H_2O$, $[Cr(NH_3)_6][Al(nta)_2]\cdot4H_2O$ and the pink product in the range of about 1500 to 1800 cm^{-1}. From the figure, only broad and very strong peak due to coordinated

-COO$^-$ groups can be detected in the spectra of the former two complexes, whereas the pink product gives an additional sharp peak. This suggests that the carboxylate groups of the former two complexes are all in coordination, while the pink product has coordinated and uncoordinated -COO$^-$ groups.

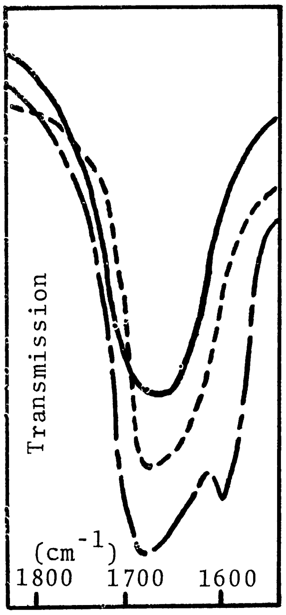

Fig. 2 IR spectra of $K_3[Al(nta)_2]\cdot 6H_2O$ (———), $[Cr(NH_3)_6][Al(nta)_2]\cdot 4H_2O$ (-----) and the pink product (—— - ——).

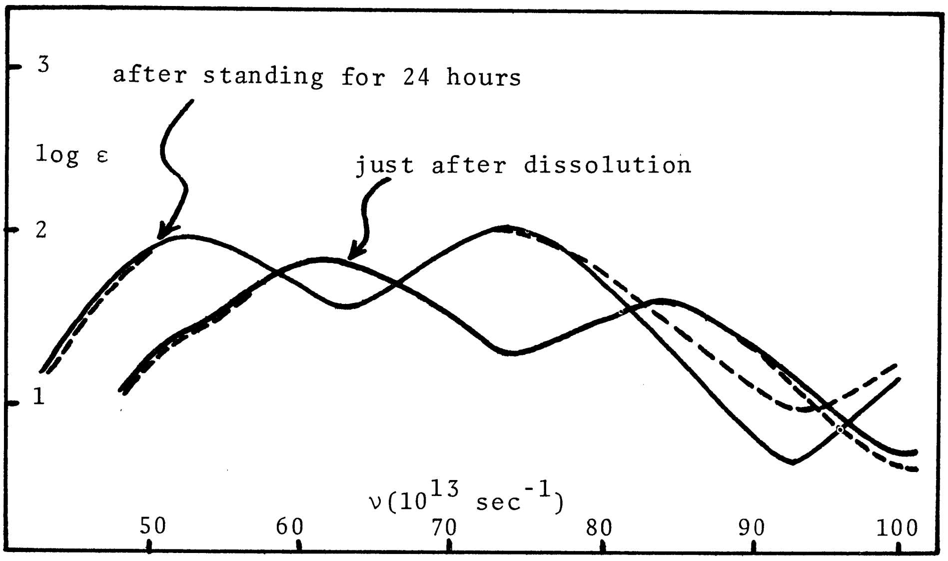

Fig. 3 Electronic spectra of trans(N)-$(NH_4)_3[Cr(nta)_2]\cdot 4H_2O$ (———) and the pink product (-----).

Electronic Spectra. Figure 3 contains the electronic spectra of trans(N)-$(NH_4)_3[Cr(nta)_2]\cdot 4H_2O$$^{2)}$ and the pink product just after dissolution in water and after standing for 24 hours. Resemblance between both spectra just after dissolution in water supports that the pink product consists of $[Cr(nta)_2]^{3-}$. It is known that $(NH_4)_3[Cr(nta)_2]\cdot 4H_2O$ after the period of standing in water undergoes gradually aquation and finally converts into $[Cr(OH)nta(H_2O)]^-$. Close similarity between both spectra after the period emphasizes that the pink product quite resembles $(NH_4)_3[Cr(nta)_2]\cdot 4H_2O$ in the reaction in aqueous medium.

Thermal Reaction Process. The foregoing results permit us to conclude that the nta initially coordinated to aluminum ion migrates to chromium ion upon heating as represented in Fig. 4. This is accompanied by variation in coordination types of the nta; namely, the coordination behavior of the nta changes to (n_1-o_2)-type toward chromium ion from (o_3)-type toward aluminum ion. Details about the migration mechanism are still unknown, but the reaction probably involves an transient intermediate in which a -COO$^-$ group in the nta functions bilaterally toward both metal ions.

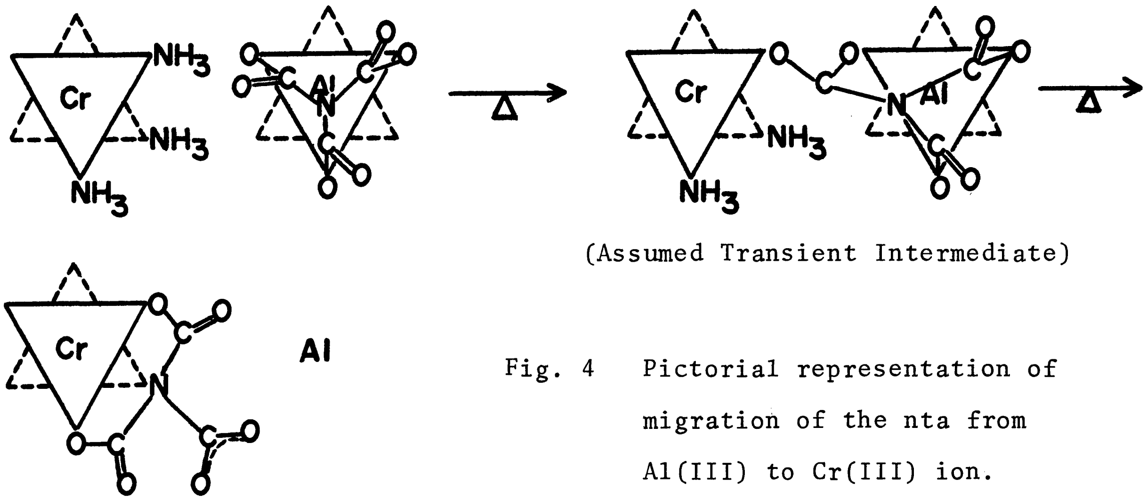

Fig. 4 Pictorial representation of migration of the nta from Al(III) to Cr(III) ion.

Being different from prior thermal reactions of metal complexes in solid-phase, the reaction of $[Cr(NH_3)_6][Al(nta)_2]\cdot 4H_2O$ described above is unique in respect to both involvement of metal substitution and occurrence of variation in coordination types of the ligands.

References

1) R. Tsuchiya, A. Uehara and E. Kyuno, Chem. Lett., 21 (1974).
2) A. Uehara, E. Kyuno and R. Tsuchiya, Bull. Chem. Soc. Japan, 40, 2317 (1967).

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