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PREPARATION OF SQUARATO-COMPLEXES AND THE THERMAL S_E REACTION THEREOF IN SOLID-PHASE*

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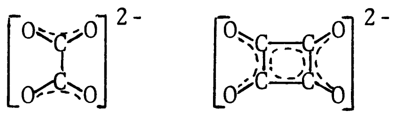
$[Cr(NH_3)_6][Al(C_4O_4)_3]$ was prepared by the reaction of $[Cr(NH_3)_6](NO_3)_3$ with $K_3[Al(C_4O_4)_3]\cdot 2H_2O$, where $C_4O_4^{2-}$ designates squarate ion. The thermal reaction of the complex in the solid-phase was investigated by means of derivatography. It was found that the squarate ion initially coordinated to Al(III) ion migrates to Cr(III) ion upon heating through the formation of a transient intermediate in which the squarate ion is coordinated bilaterally toward both metal ions; the complex is converted finally into $Al[Cr(C_4O_4)_3]$.

In the previous paper,[1)] we reported an interesting phenomenon that metal substitution (S_E reaction) takes place in the thermal reaction of a series of Cr(III)-ammine——Al(III)-oxalato double complexes in the solid-phase. We expected that the success in finding such an interesting phenomenon is attributable to the fact that the oxalate ion has, potentially, a possibility of behaving bilaterally toward both metal ions.

The present paper deals with squarate ion[2)] in place of oxalate ion in order to validate our expectation.

Squarate ion is a dianion as shown in Fig. 1 and resembles oxalate ion in some points. For example, these ions have a symmetrical planar structure[3)] and hence have a potency of functioning bilaterally toward two metal ions.



oxalate ion squarate ion

Fig. 1 Oxalate and squarate ions.

Many communications have already been published on squaric acid,[3—6)] but little is known on the coordination compounds of the acid. This is probably due to the fact that the acid has so strongly dissociating and reducing abilities[4,5)] that the metal complexes thereof can not be synthesized in ordinary or conventional manners. Thus, special regard should be taken to the preparation. We have now succeeded in preparing the metal complexes containing squaric acid.

The paper is, therefore, concerned with (1) the preparation of the squaric acid complexes and (2) the investigation on the thermal reaction thereof in the solid-phase.

Preparation of Complexes. 1) Sodium Tri(squarato)aluminate(III) Dihydrate, $Na_3[Al(C_4O_4)_3]\cdot 2H_2O$ (white). Squaric acid (10 g, 0.09 mole) synthesized by modifying the known method[5] was completely dissolved in hot water (about one litter) containing sodium hydroxide (3.5 g, 0.09 mole). Thereto, aluminum hydroxide (2.3 g, 0.03 mole) freshly prepared was added and then the mixture was boiled for about one hour with continuous stirring. White powdered insoluble precipitates were obtained, of which composition was found to be $[Al(OH)(C_4O_4)(H_2O)_3]$ (Found: C, 21.9; H, 3.2 %. Calcd: C, 22.6; H, 3.3 %.). After the precipitates were filtered off, the filtrate was concentrated to about 300 ml of its volume. The resulting solution was allowed to stand in a refrigerator. White pile-like crystals were obtained, which were recrystallized from hot water. Yield 6 g.

Found: C, 31.0; H, 1.1 %. Calcd for $Na_3[Al(C_4O_4)_3]\cdot 2H_2O$: C, 30.8; H, 0.9 %.

2) Potassium Tri(squarato)chromate(III) Dihydrate, $K_3[Cr(C_4O_4)_3]\cdot 2H_2O$ (green). Squaric acid (7.2 g, 0.063 mole) and potassium hydroxide (2.1 g, 0.037 mole) were completely dissolved in hot water (about 300 ml), and thereto potassium dichromate (VI) (2.8 g, 0.009 mole) was little by little added. The color of the solution turned to green from orange because of the reduction of Cr(VI) to Cr(III) ion. The solution thus obtained was warmed on a waterbath for about 30 min and then allowed to stand overnight, from which violet powdery insoluble precipitates were obtained. The precipitates were proved to consist of $[Cr(OH)(C_4O_4)(H_2O)_3]$ (Found: C, 20.1; H, 2.9 %. Calcd: C, 20.4; H, 3.0 %.). After the precipitates were removed off, the filtrate was neutralized with an appropriate amount of potassium hydrogen carbonate (pH 6—7). Then the solution was concentrated to 100 ml of its volume and allowed to stand in a refrigerator, from which green crystals were obtained. Recrystallization was carried out from water. Yield 2 g.

Found: C, 27.3; H, 0.6 %. Calcd for $K_3[Cr(C_4O_4)_3]\cdot 2H_2O$: C, 26.8; H, 0.7 %.

3) Hexaamminechromium(III) Tri(squarato)aluminate(III), $[Cr(NH_3)_6][Al(C_4O_4)_3]$ (yellow). Hexaamminechromium(III) nitrate (1.7 g, 0.005 mole) and sodium tri(squarato)aluminate(III) dihydrate (2.3 g, 0.005 mole) were separately dissolved in water (about 200 ml), and then the two solutions were mixed. The mixture was allowed to stand in a refrigerator, from which yellow crystals were readily obtained. The crystals could not be recrystallized because it was sparingly soluble in water, and no suitable solvent could be found. Therefore, the starting materials for use in preparing the complex should be purified beforehand.

Found: C, 28.9; H, 3.2; N, 15.8 %. Calcd for $[Cr(NH_3)_6][Al(C_4O_4)_3]$: C, 27.9; H, 3.5; N, 16.2 %.

Thermal Reaction of $[Cr(NH_3)_6][Al(C_4O_4)_3]$. Figure 2 shows the derivatogram of $[Cr(NH_3)_6][Al(C_4O_4)_3]$ measured with a derivatograph at the heating rate of 1°C/min in a nitrogen stream. As seen from the TG curve, the weight of the complex decreases slowly at 40—170°C and then rapidly at 170—195°C. The mass loss appearing in the range from 40 up to 195°C corresponds to the weight of six moles of ammonia. Two endothermic peaks successively appear in the DTA curve, which implies that the coordinated ammonia molecules are evolved in two separate steps. Further examination of the change in the TG curve of the complex was carried out at a lower heating rate (i. e., 1°C/10 min). The result is depicted in Fig. 3. It is seen that two moles

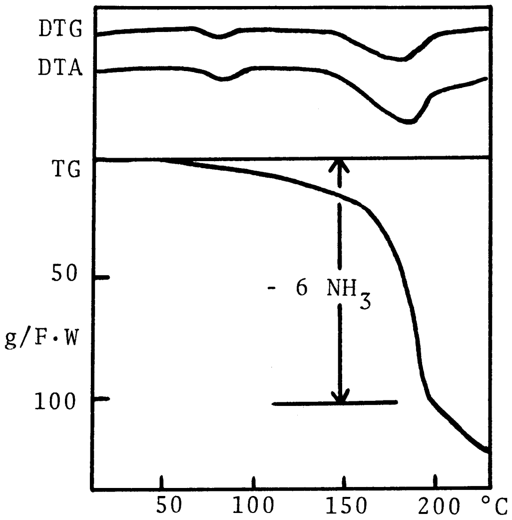


Fig. 2 Derivatogram of $[Cr(NH_3)_6][Al(C_4O_4)_3]$ (heating rate: 1°C/min)

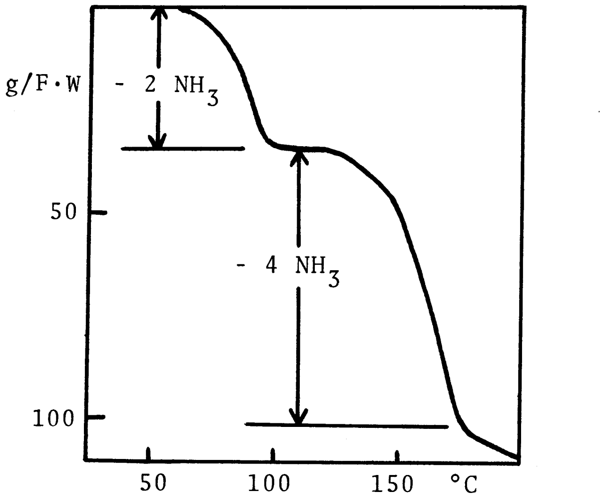


Fig. 3 TG curve of $[Cr(NH_3)_6][Al(C_4O_4)_3]$ (heating rate: 1°C/10 min)

of ammonia are first liberated at about 70—100°C and then the remaining four moles of ammonia at about 120—180°C. The color of the complex turns to green at the latter step from original yellow.

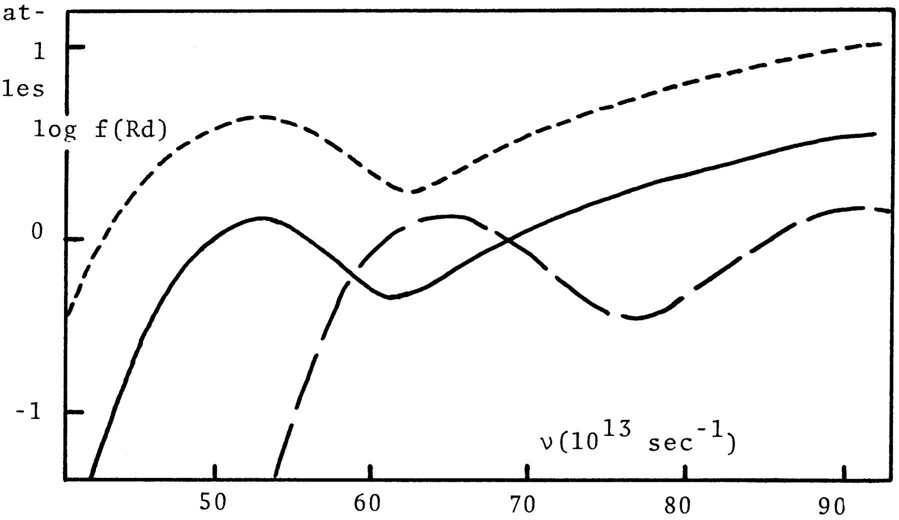


Fig. 4 Electronic spectra of $[Cr(NH_3)_6][Al(C_4O_4)_3]$ (— — — —), the green product (-------) and $K_3[Cr(C_4O_4)_3]\cdot 2H_2O$ (————).

Electronic Spectra. Figure 4 represents the electronic spectra of $[Cr(NH_3)_6][Al(C_4O_4)_3]$, the green product and $K_3[Cr(C_4O_4)_3]\cdot 2H_2O$ measured by a diffuse-reflectance method. The spectrum of $[Cr(NH_3)_6][Al(C_4O_4)_3]$ is essentially similar to that of $[Cr(NH_3)_6]^{3+}$ ion. The spectrum is gradually shifted to a lower frequency region, and finally the green product gives the same spectrum as that of $K_3[Cr(C_4O_4)_3]\cdot 2H_2O$. This indicates that the green product consists of $[Cr(C_4O_4)_3]^{3-}$ ion. The reason why the second band does not clearly appear may be ascribed to the fact that the second band is overlapped with the subsequent band due to the charge transfer from $C_4O_4^{2-}$ to Cr(III) ion.[7)]

Thermal Reaction Process. The foregoing results suggest that $[Cr(NH_3)_6][Al(C_4O_4)_3]$ evolves six moles of ammonia and is converted finally into $Al[Cr(C_4O_4)_3]$ via the following path-way:

$$[Cr(NH_3)_6][Al(C_4O_4)_3] \xrightarrow{-\ 2\ NH_3} [(NH_3)_4Cr(C_4O_4)Al(C_4O_4)_2]$$

$$\xrightarrow{-\ 4\ NH_3} Al[Cr(C_4O_4)_3]$$

In the path-way, squarate ion initially coordinated to Al(III) ion migrates to Cr(III) ion as shown in Fig. 5; viz., squarate ion is first coordinated unilaterally to Al(III) ion (Fig. 5 A), then bilaterally to both metal ions (Fig. 5 B) and finally unilaterally to Cr(III) ion (Fig. 5 C).

The reaction is very exciting since, from another point of view, it may be regarded as a kind of metal substitution of the complex in the solid-phase.

The information obtained here offers an evidence which supports our previous expectation that the occurrence of such an interesting reaction depends largely upon whether ligands used are bilateral or not.

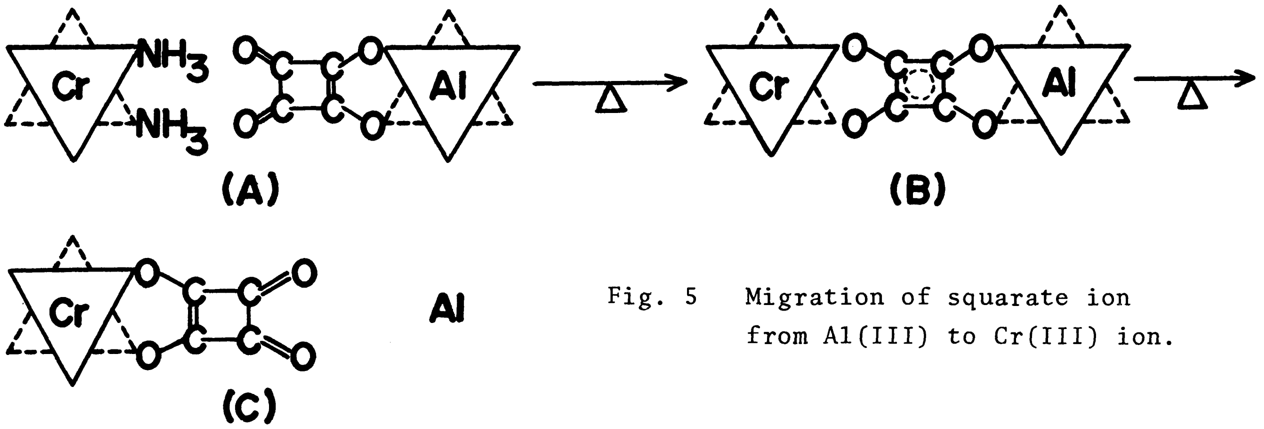


Fig. 5 Migration of squarate ion from Al(III) to Cr(III) ion.

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*) This report was presented at the 24th Symposium on Coordination Compounds of the Chemical Society of Japan, Kanazawa, October, 1974.

References

1) R. Tsuchiya, A. Uehara, and E. Kyuno, Chem. Lett., 21 (1974).

2) The general names "squaric acid" and "squarate" for 3,4-dihydroxy-3-cyclobutene-1,2-dione and its dianion have already been used in literature.[4)] For the sake of convenience, both the names will be employed throughout this paper.

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7) The spectra of the squaric acid complexes will be, in detail, published elsewhere.

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