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Formation Constants of Chromium(III) Complexes with Phthalic Acid and the Jumping Property of the Solid Complex*[1]

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Applying the continuous variation method to a mixed solution of the hexaaquochromium(III) perchlorate and phthalic acid, the complex formed in the aqueous solution was found to have mole ratios of chromium and ligand material of 1 : 1 and 1 : 3 at pH 1—2 and 3—4 respectively. The formation constants of the chromium(III) complexes with phthalic acid were determined by the pH method. The step-by-step formation constants were found to be $\log k_1 = 5.52$, $\log k_2 = 4.48$, and $\log k_3 = 2.48$ respectively. The solid chromium(III) complex with phthalic acid was also prepared. Though it was found to be an amorphous solid by X-ray diffraction measurement, the composition was close to $K_3[Cr_3(ph)_3(OH)_6(H_2O)_6]$ ($ph = C_8H_4O_4^{2-}$). A curious phenomenon was observed in the moist air; the substance in the dried state jumped, probably due to the absorption of water vapor.

The formation constants of the chromium(III) malonato and succinato complexes have been determined in an earlier publication.[1) As part of a series of studies concerning the formation constants of the chromium(III) complexes with dicarboxylic acids, the phthalato complexes were taken up in the present study. The phthalate anion will form a seven-membered chelate ring in these complexes, as in the complexes with the succinate anion. However, the former ligand has an aromatic benzene ring in itself, whereas the latter has none. Moreover, since the phthalate ion is forced to have a planar structure due to the presence of two carboxylate groups attached to the ortho-positions in a benzene ring, the phthalate anion could not so easily coordinate to a metal ion as the succinate anion. On the basis of such a presumption, the formation constants of the chromium(III) phthalato complexes were measured, and their differences from those of succinato complexes discussed.

According to the spatial specificities of the phthalate anion presented above, it was also predicted that, if it coordinates to a metal ion as a chelating agent, the complex formed will leave a considerably strong strain in it, and that, therefore, the anion can be somewhat easily bridged between two metal ions. Using the prediction resulting from the above structure, the solid complex of chromium(III) with phthalic acid was prepared.

Experimental

Continuous Variation Method. Prior to the determination of the formation constants of the complexes, the continuous variation method was used to ascertain the composition of the complex species in an aqueous solution. The necessary experiments were achieved by measuring the conductivities or the optical densities in a solution under various concentration ratios of hexaaquochromium(III) perchlorate and phthalic acid. The apparatus used was the same as that described in an earlier paper.[2)

Formation Constant Determination. The formation constants of the chromium(III) phthalato complexes were determined by the pH method also described in the earlier paper.[2) The pH value was read with a Toa Denpa pH meter, model HM-8.

Preparation of Solid Complex of Chromium(III) with the Phthalate Anion. About 20 g (*ca.* 1/10 mol) of potassium hydrogen phthalate was dissolved into 1000 m*l* of water, and to this solution there was added about 10 g (*ca.* 1/10 mol) of potassium carbonate, which is a little in excess of the amount required to neutralize the acidity of the original solution. After the reaction had ceased, about 14 g (*ca.* 1/30 mol) of chromium(III) nitrate nonahydrate was added to the solution, whereupon the pH became 9. When the residue formed in the solution was filtered off, as the filtrate was concentrated to some extent by heating it on a water-bath, a bluish-green film-like substance began to appear on its surface. If the concentration became extensively high, the gelatinous chromium(III) hydroxide was formed, disturbing the collection of the desired crops. Therefore, the heating had to cease at the earlier step in the formation of the film-like substance. It was filtered, washed with water, and dried on concentrated sulfuric acid in a desiccator.

The net yield was very small, amounting to 100 mg at best. It was insoluble in water, alcohol, ether, acetone, dioxane, toluene, nitrobenzene, and other organic solvents, though it was soluble when decomposed in strong inorganic acids and bases.

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*[1] Read at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965, and the 15th Symposium on Coordination Chemistry, Kanazawa, October, 1965.

1) H. Muro and R. Tsuchiya, This Bulletin, **39**, 1589 (1966).

2) T. Katsurai, M. Kato and K. Sone, *Kolloid Z.*, **156**, 79 (1958).

Since it was unstable in the dried state in moist air, the analysis was carried out on the sample at a constant weight after enough water vapor had been absorbed. Found: Cr, 16.30; K, 10.80%. Calcd for $K_3[Cr_3(ph)_3(OH)_6(H_2O)_6]$: Cr, 15.99; K, 12.02%.

X-Ray Diffraction Measurements. X-Ray powder diffraction measurements of the complex gave no distinct peaks, showing that it is really amorphous.

Infrared Absorption Spectra. The infrared absorption spectra of the solid complex in the dried state or in the state when water vapor was absorbed were measured with a Nippon Bunko DS-301 Infrared Spectrometer.

Results and Discussion

Continuous Variation Method. (a) The results obtained by applying the variation method, measuring the conductivity in the system of hexaaquochromium(III) perchlorate and phthalic acid, are shown in Fig. 1. The pH values of the solution were in the range of 1—2. Since a maximum peak was found at 0.5 of the mole fraction of the chromium salt in the system shown in Fig. 1, it may be considered that the principal complex formed probably has the composition of 1 : 1.

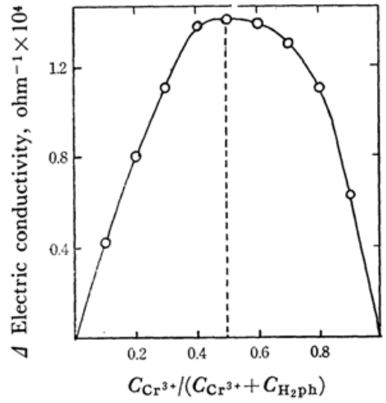


Fig. 1. Continuous variation method by the conductivity measurement.

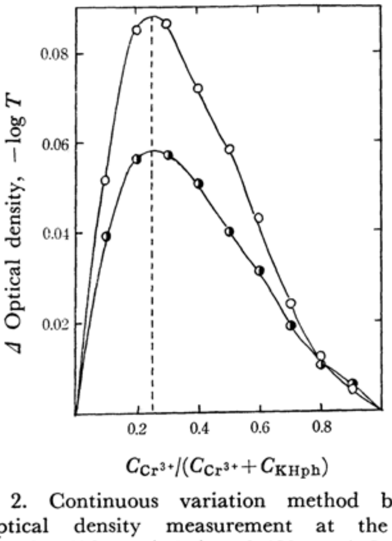


Fig. 2. Continuous variation method by the optical density measurement at the wave lengths, 570 mμ (-○-) and 420 mμ (-◑-).

(b) The results obtained by the same method using the optical density variation in the system of hexaaquochromium(III) perchlorate and potassium hydrogen phthalate at pH 2.8—3.0 are shown in Fig. 2. The optical densities were measured at two wavelengths, 570 mμ and 420 mμ, which correspond to the first and second absorption bands of the chromium(III) phthalato complex respectively. Since the maximum peak appears in the mole fraction of about 0.67 in each curve in Fig. 2, the composition of the complex formed seems to be 1 : 3.

Formation Constants. By applying the so-called Bjerrum method to the observed pH values in the same manner as in a previous paper,²⁾ the average numbers of the phthalate anion coordinated to one chromium atom, $\bar{n}$, and the reciprocal logarithm values of the concentration of a ligand free from bonding with chromium and hydrogen, p[ph^{2-}], were calculated.

The formation curve, $\bar{n}$ - p[ph^{2-}], is shown in Fig. 3.

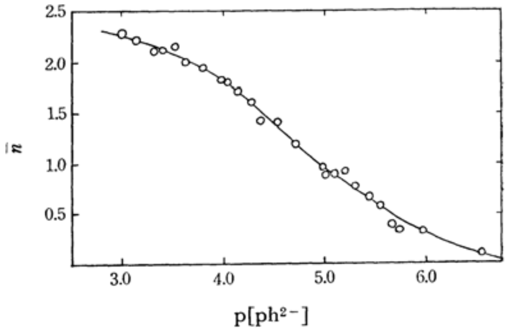


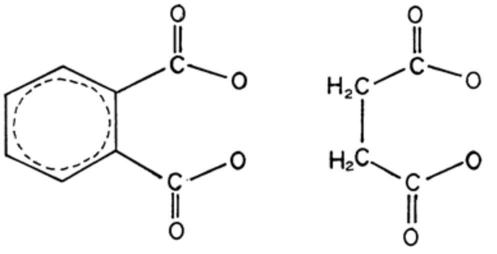
Fig. 3. Formation curve, $\bar{n}$ - p[ph^{2-}].

TABLE 1. FORMATION CONSTANTS OF CHROMIUM(III) PHTHALATO AND SUCCINATO COMPLEXES AT μ=0.1 AND 25°C

Complex	$\log k_1$	$\log k_2$	$\log k_3$	$\log K$
Phthalato-chromium(III)	5.52	4.48	2.48	12.48
Succinato-chromium(III)	6.42	4.57	2.86	13.85

By applying the successive approximation method to the tentative values of the formation constants obtained from the formation curve in the figure, the step-by-step formation constants of phthalatochromium(III) complexes were obtained. They are listed in Table 1, together with those of the corresponding succinato complexes.

The phthalate anion has a structure similar to that of the succinate anion, since both anions can



Phthalate anion Succinate anion

Fig. 4. Coordination patterns of phthalate and succinate anions.

form a seven-membered chelate ring when they coordinate to a metal as bidentate ligands, although the former contains a benzene ring in the molecule, whereas the latter does not, as Fig. 4 shows.

Since the succinate anion has no double bonds among the carbon atoms in the molecule, the seven-membered ring formed by coordination to a metal will, of course, not leave very much strain due to the free rotation between them. However, it may be expected that the coordinating ring formed by the phthalate anion will show a large strain due to the conjugated double bonds in the plane of the ligand.

It may be found in Table 1 that the formation constants of the phthalatochromium(III) complexes are smaller than those of the succinatochromium(III) complexes. Such a discrepancy in the formation constants between these two complexes may be due to a difference in the degree of strain in the coordination, described above.

Jumping of the Phthalatochromium(III) Complex. The phthalatochromium(III) complex prepared from the aqueous solution of chromium(III) nitrate and potassium hydrogen phthalate at pH 9 in the present work has the curious property of jumping when it is taken out of the desiccator and exposed to moist air.

Such jumping phenomena have already been discovered in certain organic pigments, Orient Soluble Blue and Orient Nigrosine; they have been found to be due to the absorption of water vapor by the pigments.³⁾

The fact that the jumping of the complex in the present study is also due to the absorption of water vapor has been qualitatively verified by the measurement of the infrared absorption spectra of the complex before and after the jumping.

The spectra are shown in Fig. 5, in which the appearance of a more strengthened absorption in the 3500—3100 cm^{-1} region is detected after the complex jumps.

Obviously, the desirable desorption of water vapor from the sample could be made in the desiccator after the solid complex had absorbed enough water vapor. Such experiments concerning the absorption and desorption of water vapor could be repeated several times without very much error.

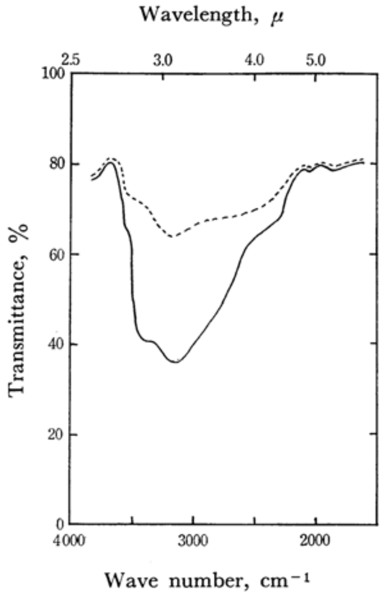


Fig. 5. Infrared absorption spectra of the complex before jumping (……) and after jumping (——).

An example of the accompanying weight change is shown below:

Dried complex		Complex after water has been absorbed	Weight change (%)
0.2152 g	in moist air ⟶	0.2423 g	+0.0271 g (+11.3%)
	in the desiccator		−0.0245 g (−10.1%)
0.2178 g	in moist air	0.2410 g	+0.0232 g (+9.7%)
	in the desiccator		−0.0245 g (−10.2%)
0.2165 g			

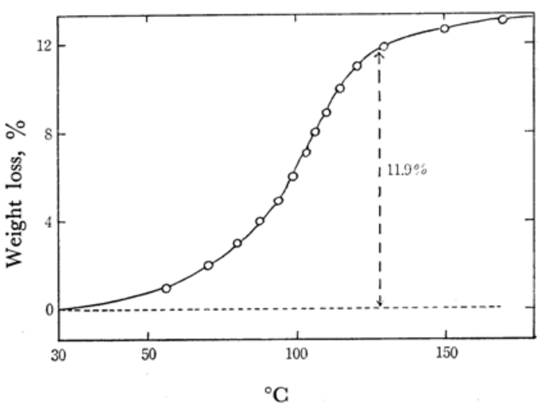


Fig. 6. Thermogravimetric curve for the complex.

It is indicated in the above experiments that the amount of water vapor absorbed or desorbed reversibly is about 10—11%, which is close to the 11.6% figure representing the weight loss percentage based on the reaction:

$$K_3[Cr_3ph_3(OH)_6(H_2O)_6] \rightarrow K_3[Cr_3ph_3(OH)_3].$$

On the other hand, the complex which had absorbed enough water vapor was thermally decomposed with a Shimadzu Thermano-Balance. The thermogravimetric curve is shown in Fig. 6. When the complex was picked up at the intermediate decomposition step, where the weight loss equals the amount of water vapor involved with the reversible desorption, and was exposed in air, the same jumping phenomenon was observed as in the case of the complex taken out of a desiccator.

The assumption that a solid complex absorbing water vapor with a 1 : 1 mole ratio has a possible composition of $K_3[Cr_3ph_3(OH)_6(H_2O)_6]$ seems reasonable in view of the above experiments. The complex with a mole ratio of 1 : 2 or 1 : 3 could not be obtained in either the solid state or in an aqueous solution.