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Formation Constants of Maleatochromium(III) Complexes and Some Properties Thereof in the Solid State*[1]

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The formation constants of the chromium(III) complexes with maleic acid have been determined by the pH method to be $\log k_1 = 5.4 \pm 0.1$, $\log k_2 = 3.0 \pm 0.1$, and $\log k_3 = 1.9 \pm 0.2$ at an ionic strength of $\mu = 0.1$ and at 25°C. We also attempted to prepare the solid of the chromium(III) complex with maleic acid. Though it was an amorphous solid to X-ray diffraction measurement, its composition was presumed to be $[Cr(mal^{*2})(OH)(H_2O)_3]$. After it had been dried in a desiccator for a few days, when it was exposed to moist air we observed the curious phenomenon that the solid was made jumping due to the absorption of water vapor.

The formation constants of the chromium(III) complexes with succinic and with phthalic acids have been reported by one of the present authors in earlier papers.[1,2] The curious jumping property of the latter complex in the solid state after it had been dehydrated was also noted.[2] In continuation of the above works, the formation constants of chromium(III) complexes with maleate have been determined. All the three anions described above can make similar coordination bonds to chromium(III) through the seven-membered chelate ring; there is only a fine structural difference originating from the ligand molecules themselves. The effect of such differences in the structure upon the formation constants of the chromium(III) complexes concerned will be discussed below.

Experimental

Formation Constant Measurement. The formation constants were determined by means of pH measurements in a mixed solution of hexaaquochromium(III) perchlorate and maleic anhydride at an ionic strength of $\mu = 0.1$ and at 25°C in a manner similar to that described in an earlier paper.[2] The maleic anhydride used as a ligand material was of a special grade and had been obtained from Wako Pure Chemical Industries, Ltd.

Attempt of Preparation of the Solid Maleatochromium(III) Complex. We attempted to prepare the maleatochromium(III) complex in the solid state by the procedure reported in an earlier paper.[2] To a mixed solution of 6 g (1/60mol) of chromium(III) nitrate nonahydrate and 5 g (1/20 mol) of maleic anhydride, we added 13 g (1/7 mol) of ammonium carbonate; the resulting solution was then evaporated to some extent until the film-like substance covering the surface of the solution began to appear. Then it was scooped on the filter and dried in the desiccator. About 2 g of the product were obtained. The product was amorphous to X-ray diffraction measurements.

The product showed the curious property of jumping when it was exposed to moist air, just as the phthalatochromium(III) complex did.[2] The analysis of the sample after it had absorbed enough water vapor gave the chromium content of 21.51%, a value of which is in good agreement with the calculated value, 21.93%, for the chemical formula, $[Cr(mal)(OH)(H_2O)_3]$.

Results and Discussion

Comparison of the Formation Constants of Maleatochromium(III) Complexes with Those of Phthalato- and Succinatochromium(III) Complexes. The relevant values of the first and second acid dissociation constants of maleic acid required for determining the formation constants of the complexes were taken from the literature—$pK_1 = 1.92$[3] and $pK_2 = 5.79$[4] respectively at an ionic strength of $\mu = 0.1$ and at 25°C.

The methods of calculating the average number of coordinated maleate anions as ligands per gram-ion of the chromium, $\bar{n}$, and the concentration of the non-coordinated anions, $p[A^{2-}]$, in solution, are the same as those described in an earlier paper.[5] The plots of $\bar{n}$ *vs.* $p[A^{2-}]$ for the maleatochromium(III) system are shown in Fig. 1, together with those for the succinato- and phthalatochromium(III) systems.

By applying the successive approximation method to the tentative values of the formation constants

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*[2] mal=maleate anion.

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

2) K. Higashi, K. Hori and R. Tsuchiya, *ibid.*, **40**, 2569 (1967).

3) N. E. Topp and C. W. Davies, *J. Chem. Soc.*, **1940,** 87.

4) M. Yasuda, K. Yamasaki and H. Ohtaki, This Bulletin, **33**, 1067 (1960).

5) K. Nagata, A. Umayahara and R. Tsuchiya, *ibid.*, **38**, 1059 (1965).

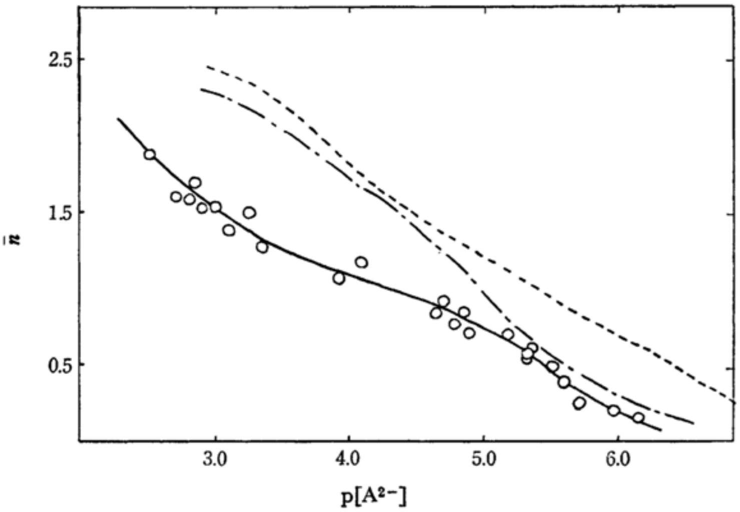

Fig. 1. Formation curve, $\bar{n}$ *vs.* p[A^{2-}].
——, in chromium(III)-maleate system
----, in chromium(III)-succinate system
-—-, in chromium(III)-phthalate system

TABLE 1. THE FORMATION CONSTANTS OF SUCCINATO-, PHTHALATO- AND MALEATOCHROMIUM(III) COMPLEXES, AT $\mu=0.1$ AND 25°C

	$\log k_1$	$\log k_2$	$\log k_3$	pK_1	pK_2	Ref.
Succinato complex	6.42	4.57	2.86	4.00	5.21	1)
Phthalato complex	5.52	4.48	(2.5)	2.76	4.92	2)
Maleato complex	5.4	3.0	(1.9)	1.92	5.79	

(The numerals in parentheses are the values estimated by extrapolating the formation curve.)

obtained from the formation curve shown in Fig. 1, the step-by-step formation constants were obtained; they are listed in Table 1, together with those of the succinato- and phthalatochromium(III) complexes.

It is obvious from Table 1 that the formation constants of the maleato and phthalato complexes are rather smaller than those of the succinato complexes. This is due to the structural differences among the ligand molecules used.

The phthalate and maleate anions may be forced to hold the planar structure in a complex formation because of the presence of a benzene ring in the former and that of the double bond between two carbon atoms instead of the benzene ring between two carboxylate groups in the latter. Since the distance between two oxygen atoms which can coordinate to the metal ion in these two carboxylate anions is presumed to be about 1.6 Å on the basis of the crystal structure of the maleic acid,[6] a remarkable strain may be predicted to occur in the chelate formation when they coordinate to a metal ion using the above two oxygens as the bidentate ligand.

On the other hand, since the succinate anion[7] has neither a benzene ring nor a double bond between two carbon atoms within itself, the free rotation of the ethylene linkage placed between two carboxylate groups is possible without any steric hindrance. As a result, it may not always make a planar coordination structure. Therefore, in this case, little strain should appear in the chelate formation. It may be concluded that the difference in the original structure in the ligand coordinated to metal as mentioned above is the main contribution to the lower stability of the phthalato and maleato complexes than that of the succinato complexes.

When we compare the formation constants of the phthalato and maleato complexes in Table 1, we find that the latter are relatively smaller than the former. The phthalate and maleate must commonly form similar seven-membered planar chelate rings as a result of the double-bond character involved in their chelate rings.

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6) M. Shahat, *Acta Cryst.*, **5**, 763 (1952).

7) J. S. Broadley, D. W. J. Cruickshank, J. D. Morrison, J. M. Robertson and H. M. M. Shearer, *Proc. Roy. Soc.* (*London*), **251A**, 441 (1959).

Since, while the phthalate anion has a benzene ring, the maleate one has none, the double-bond character between the two carbon atoms combining with two carboxylate groups seems to be weaker in the former than in the latter. This results in the lesser electronic density at the oxygen atoms coordinating to metal in the latter than in the former. Therefore, it may be suggested that the basicity of the maleate anion is rather smaller than that of the phthalate. The values of the total acid dissociation constants of these acids given in Table 1 support this idea.

In short, the lesser stability of the maleato complexes than that of the phthalato complexes can be well explained by the facts that the acid dissociation constant of the maleic acid is smaller than that of the phthalic acid.

Jumping Property of the Solid Maleatochromium(III) Complex. The solid maleatochromium(III) complex prepared and dried in a desiccator showed jumping when it was exposed to moist air, as in an earlier experiment.[2] The fact that the phenomena took place as a result of the absorption of water vapor was ascertained by the presence of a stronger and broader absorption band in the range of 3200—3600 cm^{-1} of the IR spectra after jumping than before jumping.

It was observed that, even after the sample had absorbed water vapor enough to cause it to cease jumping, the jumping property re-appeared when it was again exposed to moist air.

The weight loss of the sample which had absorbed water vapor in the moist air and had ceased jumping was measured by the thermobalance; it is plotted in Fig. 2. The figure shows that a metastable dehydrated compound is formed by a weight loss of 20—24% at about 200°C; this is approximately consistent with the calculated value, 22.8%, for the following reaction:

$$[Cr(mal)(OH)(H_2O)_3] \xrightarrow{-2H_2O} [Cr(mal)(OH)(H_2O)].$$

It was also found that the sample which had thermally lost the water vapor in the amount corresponding to the expression in this equation began jumping again in the moist air, as in the case of the phthalatochromium(III) complex in the solid state reported on in an earlier paper.[2]

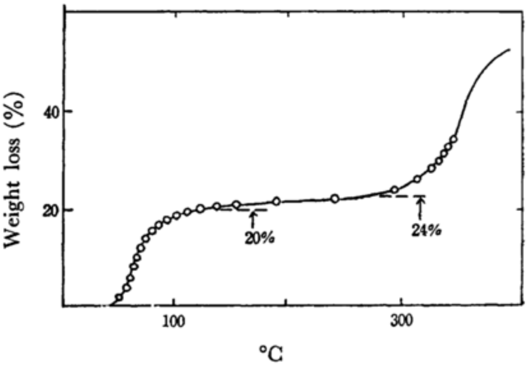

Fig. 2. Thermogravimetric curve of the solid maleatochromium(III) complex.