NOTES

Formation Constants of Malonato- and Succinatochromium(III) Complexes*[1]

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In comparison with several reports[1,2] on formation constants in bivalent metal complexes with malonic and succinic acids, there have been no papers on those in tervalent metal complexes excepting for some rare earth metal complexes[3] with these ligands.

The formation constants of chromium(III) complexes with the oxalate ion have been reported in an earlier paper[4] by one of the present authors. In continuation of the above work, the formation constants of chromium(III) complexes containing the malonate and succinate anions as a ligand have been determined; the relationship between the stability and stereostructure among these complexes, including the oxalate complexes, will be discussed in the present work.

Experimental

In a manner similar to that described in a previous paper,[4] the formation constants were determined by means of pH measurements in solutions containing the hexaaquochromium(III) perchlorate and either malonic or succinic acid at the ionic strength, μ, of 0.1 at 25°C.

The preparation and analysis of the hexaaquochromium(III) perchlorate were also carried out according to procedures similar to those in the previous paper.[4] The malonic and succinic acids used were of an analytical reagent grade and were from Nakarai Chemicals, Ltd., and Wako Pure Chemical Industries, Ltd., respectively.

Results

The values of the acid dissociation constants of malonic and succinic acids required for the determination of formation constants of their complexes were taken from the literature.*[2] The method of calculating the average number of corrdinated carboxylate anions as ligand per gram-ion of the chromium(III) ion, $\bar{n}$, and the method of calculating the concentration of non-coordinated one, $[A^{2-}]$, in solutions, are the same as those described in the previous paper.[4] The plots of $\bar{n}$ vs. $p[A^{2-}]$ for both malonato- and succinatochromium(III) systems are shown in Fig. 1.

By applying the successive approximation method to the tentative values of the formation constants obtained from the formation curve shown in Fig. 1, the stepwise formation constants of both

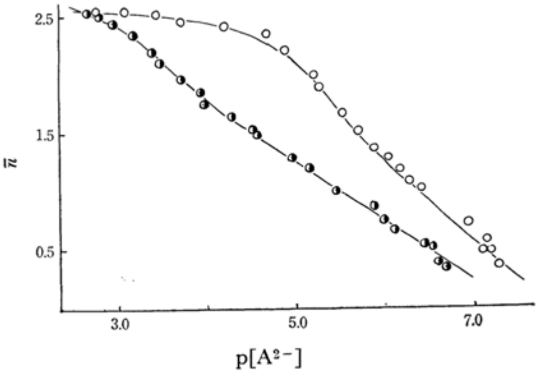

Fig. 1. The formation curve, $\bar{n} \sim p[A^{2-}]$.

—○— Malonatochromium(III) complex

—◑— Succinatochromium(III) complex

TABLE I. THE FORMATION CONSTANTS OF OXALATO-, MALONATO- AND SUCCINATOCHROMIUM(III) COMPLEXES, AT $\mu=0.1$ AND 25°C

	$\log k_1$	$\log k_2$	$\log \mathrm{k}_3$	$\log k_1k_2k_3$
Oxalato complex	5.34	5.17	4.93	15.44
Malonato complex	7.06	5.79	3.30	16.15
Succinato complex	6.42	4.57	2.86	13.85

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*[1] Presented at the 17 th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) M. Bobtelsky and J. Bar-Gadda, *Bull. Soc. Chim. France,* **1953**, 276.

2) J. Schubert and A. Lindenbaum, *J. Am. Chem. Soc.*, **74**, 3529 (1952).

3) E. Gelles and G. H. Nancollas, *Trans. Faraday Soc.*, **52**, 680 (1956).

4) K. Nagata, A. Umayahara and R. Tsuchiya, This Bulletin, **38**, 1059 (1965).

*[2] The first and second acid dissociation constants of malonic acid, $pK_1=2.76$ and $pK_2=5.29$, and those of succinic acid, $pK_1=4.00$ and $pK_2=5.21$, are cited from M. Yasuda, K. Yamasaki and H. Ohtaki, This Bulletin, **33**, 1067 (1960).

malonato- and succinatochromium(III) complexes were obtained; they are listed in Table I, together with those of the oxalatochromium(III) complexes reported previously⁴⁾ by one of the present authors.

Discussion

It may be seen from Table I that the stepwise formation constants, log k_1 and log k_1k_2, of the chromium(III) complexes decrease in the order: malonato$<$succinato$<$oxalato. This phenomenon will be discussed below.

First, one of the main factors controlling the difference in stability among these complexes may be a bond angle, like O–Cr–O, in its own chelate ring. The oxalate ion can usually form a five-membered chelate ring with a central chromium(III) ion, whereas the malonate and succinate ions can form six- and seven-membered rings with the same metal ion. Thus a O–Cr–O bond angle in a chelate ring may be expected to become larger as the size of the ring increases. Despite the above intuitive prediction, however, if the structure of the oxalatochromium(III) complex appearing in the literature⁵⁾ is compared with schematic structure of malonato- or succinatochromium(III) complex which is depicted by the aid of the bond angles and bond lengths reported for the former, it may be presumed that the bond angle, O–Cr–O, in these complexes does not deviate so greatly from rectangular as to have a vital effect on the difference in stability among these complexes.

Consequently, the most important factors determining the stability of these complexes seem to be the entropy and enthalpy changes brought about by the formation of these complexes.

The first factor is the entropy change in the complex formation. The degree of freedom of a molecule or ion becomes larger as the carbon chain in the acids becomes longer. Therefore, when the dicarboxylate anions coordinate to metal ions, the degree of the freedom of the anions decreases, depending upon the length of the carbon chain in the ligand. Thus, closely related to the above effect on the entropy change, the stability of complexes may be expected to decrease in the order: oxalato$>$malonato$>$succinato.

The results obtained in this study show that the stepwise formation, and also the overall formation constants of malonato complexes are larger than those of succinato complexes; such a stability sequence may, therefore, be reasonably explained in terms of the entropy change mentioned above. However, as this entropy factor alone may not give a complete answer to the stability order measured in the case of the oxalato complex, another factor must also be taken into account.

Since the overall acid dissociation constants of oxalic, malonic and succinic acids, pK_1+pK_2, are 4.98,⁴⁾ 8.05*² and 9.21*² respectively, the basicity of the oxygen atoms in carboxylate groups which can coordinate to a metal ion seems to be the smallest in oxalic acid, a little larger in malonic acid, and the largest in succinic acid. Although the basicity of the donor atoms is not the only factor in deciding the enthalpy change upon the coordination of these dicarboxylic acids with chromium(III) ion, it seems to be one of the most effective factors. Thus, the enthalpy change may be presumed to decrease in the order: succinato$>$malonato$>$oxalato. In the light of the enthappy change, only the stabilities of these complexes should range in the same order.

However, so far as log k_1 and log k_1k_2 are concerned, the stability order obtained here is: malonato$>$succinato$>$oxalato. This finding will be explained below.

Since the difference in the acid dissociation constants between the malonic and succinic acids is really smaller than that between the oxalic and malonic or succinic acid, the stability order in the malonato and succinato complexes seems to be not very much affected by the enthalpy change, but to depend mainly upon the entropy change, as has been assumed above, whereas the smaller stability of the oxalato complex than that of the malonato or the succinato complex is thought to be mainly due to the differences in the enthalpy effect among these complexes. In evaluating the above two main factors which may control the first and second stepwise stability constants of the complexes treated in this paper, it should perhaps be emphasized that an extra stability of the malonato complex over the succinato one is assumed to be responsible for the larger loss of entropy in the complex formation of the latter than in that of the former; the fact that the stability of the succinato complex is a little larger than that of the oxalato complex can be explained on the assumption that the enthalpy decrease accompanying the formation of the former is larger than that accompanying the latter's formation.

On the other hand, the third stepwise formation constant is largest in the oxalato complex and then descreases in the order: malonato$>$succinato complexes. This shows that the stepwise formation constants of the oxalato complex do not decrease so markedly as those of malonato or succinato complexes, as is shown in Table I. When the overall formation constants are arranged, the stability order is given as: malonato$>$oxalato$>$succinato. The trend in stepwise formation constants among the complexes involved in this work may be explained in terms of the concept of steric interaction existing among ligand molecules coordinated to a metal ion; the nearly planar structure of the oxalate ion is still held in the complex formation, whereas in the cases of both the malonate

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5) J. N. Van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **4**, 35 (1951).

and succinate anions it is possible for the mutual steric hindrance to occur among coordinated ligands as a result of their larger chelate rings.

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