BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 3416—3418 (1968)

# Formation Constants of Chromium(III) Complexes with (N, N)-, (O, O)- and (N, O)-Type Ligands, and Their Relationship to Structure*1

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(Received March 15, 1968)

Formation constants of chromium(III) complexes with $\beta$-alanine, anthranilic acid, picolinic acid and 8-hydroxyquinoline, being all (N, O)-type bidentate chelate ligands, were determined by the pH method at an ionic strength $\mu=0.1$, and at 25°C. The formation constants are $\log k_1=9.69$ for $\beta$-alanine, $\log k_1=4.35$ and $\log k_2=3.67$ for anthranilic acid, $\log k_1=4.76$, $\log k_2=4.38$ and $\log k_3=4.55$ for picolinic acid and $\log k_2=9.76$ and $\log k_2=8.48$ for 8-hydroxyquinoline, respectively. The relationships between the formation constants of the complexes and the acid dissociation constants of the chelate ligands were discussed, including those for glycine and $\alpha$-alanine complexes, and those, in addition, for the complexes with several (N, N)- and (O, O)-type ligands reported in a preceding paper.

Several papers have been previously published by the present authors on the formation constants of chromium(III) complexes, for example, with dicarboxylic acids such as oxalic,1) malonic,2) succinic,2) phthalic3) and maleic4) acids as (O, O)-type ligands, with ethylenediamine5) as an (N, N)-type ligand and glycine and $\alpha$-alanine6) as (N, O)-type ligands.

In continuation of the studies on (N, O)-type ligands, the formation constants of chromium(III) complexes with $\beta$-alanine, anthranilic acid, picolinic acid and 8-hydroxyquinoline were determined at 25°C and $\mu=0.1$, and the relationships among the formation constants of the (N, O)-type complexes presented here and those of (N, N)- and (O, O)-type complexes already published are discussed.

## Experimental

**Materials.** Picolinic acid and $\beta$-alanine were of analytical reagent grade from Nakarai Chemicals Co., Ltd., and anthranilic acid and 8-hydroxyquinoline were of guaranteed special grade from Katayama Chemicals Co., Ltd.

**Determination of Formation Constants.** The formation constants of the complexes were determined by the pH method used in previous papers.1-6) Solutions containing various concentrations of hexaaquochromium(III) perchlorate and each ligand described above were kept in a thermostat at 25°C; the ionic strength $\mu$ was adjusted to 0.1 by adding an appropriate amount of sodium perchlorate. When equilibrium was attained after one month or more, the pH of the solution was measured with a Toa Denpa pH meter, model HM-8, and the formation constants calculated.

## Results

**Acid Dissociation Constants of the Chelate Ligands.** The acid dissociation constants of $\beta$-alanine, anthranilic acid and 8-hydroxyquinoline

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[*1] Presented at the 10th International Conference on Coordination Chemistry, Nikko, September, 1967.

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

2) H. Muro and R. Tsuchiya, *ibid.*, **39**, 1589 (1966).

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

4) T. Tomita, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 1130 (1968).

5) M. Ohta, H. Matsukawa and R. Tsuchiya, *ibid.*, **37**, 692 (1964).

6) H. Matsukawa, M. Ohta, S. Takata and R. Tsuchiya, *ibid.*, **38**, 1235 (1965).

TABLE 1. THE FORMATION CONSTANTS OF THE CHROMIUM(III) COMPLEXES WITH (N, O)-TYPE CHELATE LIGANDS AT $\mu=0.1$ AND AT 25°C

| Ligand | $\log k_1$ | $\log k_2$ | $\log k_3$ | $pK_1$ | $pK_2$ | Ref. |
|---|---|---|---|---|---|---|
| Glycine | 8.62 | 7.65 | 5 | 2.43 | 9.62 | 6 |
| $\alpha$-Alanine | 8.53 | 7.44 | 5.94 | 2.53 | 9.59 | 6 |
| $\beta$-Alanine | 9.69 | — | — | 3.53 | 10.08 | * |
| Anthranilic acid | 4.35 | 3.67 | — | 1.97 | 4.79 | * |
| Picolinic acid | 4.76 | 4.38 | 4.55 | 1.60 | 5.44 | * |
| 8-Hydroxyquinoline | 9.76 | 8.48 | — | 4.92 | 9.23 | * |

* the present work

were determined by titrating aqueous solutions containing the ligand alone with hydrochloric acid or sodium hydroxide solution under $\mu=0.1$ and at 25°C, and they were calculated by applying the following equations,[7]

$$pK_1 = pH - \log\left(\frac{C}{A-[H^+]} - 1\right)$$

or

$$pK_2 = pH - \log\left(\frac{C}{B-[OH^-]} - 1\right)$$

where $C$ is the total concentration of the chelate ligand, $A$ and $B$ are the concentrations of the hydrochloric acid and sodium hydroxide solutions calculated from their titres, respectively, and $pK_1$ and $pK_2$ are the acid dissociation constants of the ligand. The values of $[H^+]$ and $[OH^-]$ were calculated by applying the activity coefficient of hydrogen ion at $\mu=0.1$, $\gamma=0.83$,[8] to its activity obtained by pH measurement.

The acid dissociation constants of $\beta$-alanine, anthranilic acid and 8-hydroxyquinoline were determined in the manner described above, whereas those of picolinic acid were taken from the literature.[9] These values are all listed in Table 1, as well as those of glycine and $\alpha$-alanine for comparison, together with the values of the formation constants of the complexes concerned.

**Formation Constants of Chromium(III) Complexes with (N, O)-Type Chelate Ligands.** The method used in determining the formation constants of the chromium(III) complexes with $\beta$-alanine, anthranilic acid, picolinic acid and 8-hydroxyquinoline as (N, O)-type chelate ligands was the same as used for the glycine and $\alpha$-alanine complexes.[6]

By combining the values of the acid dissociation constants of the respective chelate ligands and the measured pH values with the total concentrations of the chromium ion used, of the chelate ligand concerned and of the ionizable hydrogen, the average numbers of ligands coordinated to each chromium ion, $\bar{n}$, and the reciprocal logarithmic values of the free ligand, $p[A^-]$, were calculated. The formation curves, $\bar{n}-p[A^-]$, for the (N, O)-type complexes with picolinic acid, 8-hydroxyquinoline, $\beta$-alanine and anthranilic acid, together with those of glycine and $\alpha$-alanine, are shown in Fig. 1.

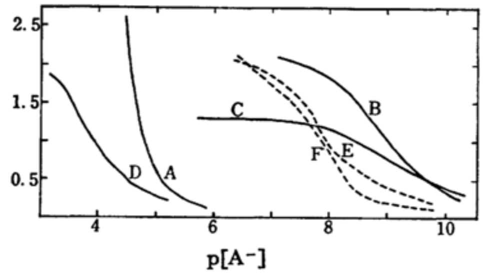

Fig. 1. Formation curves for (N, O)-type chromium(III) complexes.
A, Picolinic acid B, 8-hydroxyquinoline
C, $\beta$-Alanine D, Anthranilic acid
E, Glycine F, $\alpha$-Alanine

## Discussion

As given in Table 1, the first and second stepwise formation constants of the complexes, $\log k_1$ and $\log k_2$, decrease in the following order; 8-hydroxyquinoline > $\beta$-alanine > glycine > $\alpha$-alanine > picolinic acid > anthranilic acid. This order runs parallel to the decreasing order of the second acid dissociation constants of these ligands, $pK_2$, except for 8-hydroxyquinoline.

Although a general linear relationship between the logarithms of the formation constants, $\log k_1$, and the reciprocal logarithms of the acid dissociation constants, $pK_2$, as expressed by

$$\log k_1 = \alpha pK_2 + C,$$

where $\alpha$ and $C$ are constants, has been proposed by

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[7] F. Basolo and Y. T. Chen, *J. Am. Chem. Soc.*, **76**, 953 (1954).

[8] J. Kielland, *ibid.*, **59**, 1675 (1937).

[9] H. H. G. Jellinek and J. R. Urwin, *J. Phys. Chem.*, **58**, 548 (1954); K. Suzuki, M. Yasuda and K. Yamasaki, *ibid.*, **61**, 229 (1957).

Irving and Rossotti,[10,11] such a relationship has not always been strictly applied to many complexes, as pointed out by Jones *et al.*[12] Nevertheless, so far as both copper(II)[13] and iron(III)[14] complexes forming five-membered chelate ring with glycine and its several derivatives as (N, O)-type bidentate ligands are concerned, approximately linear relationships between $\log k_1$ and $\mathrm{p}K_2$ can be obtained, respectively.

The values of the first stepwise formation constants of the complexes listed in Table 1 are plotted against $\mathrm{p}K_2$ in Fig. 2, including those concerning chromium(III) asparagine and glycylglycine complexes.[*3] Of these complexes, so far as glycine, α-alanine, asparagine, glycylglycine and picolinic acid, which can form five-membered chelate rings with chromium(III), are concerned, the values of $\log k_1$ against $\mathrm{p}K_2$ fall approximately on a straight line, as shown in Fig. 2.

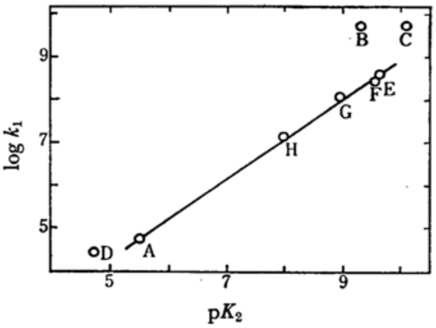

Fig. 2. Relationships between $\log k_1$ and $\mathrm{p}K_2$ in (N, O)-type complexes.
A, Picolinic acid B, 8-hydroxyquinoline
C, β-Alanine D, Anthranilic acid
E, Glycine F, α-Alanine G, Asparagine
H, Glycylglycine

This fact may mean that, in these cases, the chelating tendency is not dependent upon the presence of a side-chain or end-chain in these ligands, but mainly upon the magnitude of their $\mathrm{p}K_2$ values.

On the other hand, the first stepwise formation constants of the chromium(III) complexes with β-alanine and anthranilic acid, as shown in Fig. 2, deviate slightly from the straight line obtained above. This may be due to the six-membered chelate ring formation of these two ligands, which differs from glycine and its derivatives in forming five-membered chelate rings with the metal.

It has been reported by Bjerrum[11] that the values of $\log k_1/\log k_{\mathrm{H}}$ are almost constant for each complex of silver(I), mercury(II), copper(II) and zinc(II) ions with various amines, where $k_{\mathrm{H}}$ is the acid formation constant.

Now, putting the values of the differences, $\varDelta = \log k_1 - \mathrm{p}K_2$, on the straight line, the relationships shown in Fig. 3 are obtained.

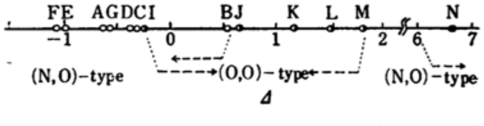

Fig. 3. The values, $\varDelta = \log k_1 - \mathrm{p}K_2$, for (N, N)-type (●), (N, O)-type (○) and (O, O)-type (◑) complexes.
A, Picolinic acid B, 8-hydroxyquinoline
C, β-Alanine D, Anthranilic acid
E, Glycine F, α-Alanine G, Asparagine
I, Maleic acid J, Phthalic acid
K, Succinic acid L, Oxalic acid
M, Malonic acid N, Ethylenediamine

The values, Δ, for the chelate ligands which can form a stronger coordinate bond with chromium than hydrogen, are placed on the right-hand side of this line, while those forming a weaker coordinate bond with chromium are placed on the left-hand side, and those which have comparable coordination tendencies toward both chromium and hydrogen are placed in the middle region of this line between the above two. Thus, their positions on the line are arranged in the order of (N, N)-, (O, O)- and (N, O)-type complexes from the right to the left. Even though values of $\log k_1$ of the (N, O)-type complexes are in the intermediate region between those of the (N, N)- and (O, O)-type complexes, the values, Δ, referred to the (N, O)-type complexes fall within a small range on the extreme left side of this line.

This may be explained by the fact that the values of $\mathrm{p}K_2$ in (N, O)-type ligands, 8 to 10, except for picolinic and anthranilic acids, are not only strikingly higher than those in (O, O)-type ligands, 4 to 5, but also rather close to those in (N, N)-type ligands, about 10. Such a similarity in values of $\mathrm{p}K_2$ in both (N, N)- and (N, O)-type ligands is reasonably expected, since the second acid dissociation will be, in common, concerned with the liberation of a proton from an amido group in (N, N)- and (N, O)-type ligands, whereas it will be concerned with the liberation of a hydrogen ion from a carboxyl group in (O, O)-type ligands.

That the values of Δ are found as slightly negative in (N, O)-type ligands suggests that the α-amino monobasic acids do not coordinate so strongly to chromium as to hydrogen.

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[10] H. Irving and H. Rossotti, *Acta Chem. Scand.*, **10**, 72 (1956).

[11] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[12] J. G. Jones, J. B. Poole, J. C. Tomkinson and R. J. P. Williams, *J. Chem. Soc.*, **1958**, 2001.

[13] B. R. Rabin, *Trans. Faraday Soc.*, **52**, 1130 (1956).

[14] D. D. Perrin, *J. Chem. Soc.*, **1958**, 3125.

[*3] The first stepwise formation constants and the second acid dissociation constants of these chromium(III) complexes are $\log k_1 = 8.2$ and $\mathrm{p}K_2 = 8.85$, respectively, for asparagine and $\log k_1 = 7.2$ and $\mathrm{p}K_2 = 8.00$ for glycylglycine, which will be published elsewhere.