The Formation Constants of Chromium(III)-Glycinato and α-Alaninato Complexes*

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Few reports on the formation constants of chromium(III) complexes have been published. In their own preceding papers the present authors have discussed the formation constants of chromium(III) complexes with ethylenediamine, the simplest chelating agent coordinating by two nitrogen atoms,[1] and those with oxalate ion, the simplest chelating agent coordinating by two oxygen atoms.[2]

Glycine, the simplest α-amino acid, is the intermediate chelating agent between ethylenediamine and oxalate ions from the structural point of view. In the present study the formation constants of chromium(III) complexes with glycine and α-alanine will be determined.

Experimental

Hexaaquochromium(III) Perchlorate.—The preparation of this salt and the method of the analyses of chromium and free perchloric acid were the same as those described in a preceding paper.[2] The compositions of the crystalline salts used for chromium(III) glycinato and α-alaninato complexes respectively were as follows:

* Read at the 13th Symposium on Coordination Compounds of the Chemical Society of Japan, Nagoya, October, 1963.

1) M. Ohta, H. Matsukawa and R. Tsuchiya, This Bulletin, 37, 692 (1964).

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

$[Cr(H_2O)_6](ClO_4)_3$, 45.61 mol.%;
$HClO_4$, 54.39 mol.%
$[Cr(H_2O)_6](ClO_4)_3$, 55.37 mol.%;
$HClO_4$, 44.63 mol.%

Glycine and α-Alanine.—The glycine used was a guaranteed reagent, and α-alanine was a reagent of the highest commercial grade.

Procedure.—The formation constants were determined by a pH method similar to that used in a preceding paper.[2] A mixed solution of hexaaquochromium(III) perchlorate and glycine or α-alanine, the ionic strength of which was adjusted to 0.1 by adding sodium perchlorate, was kept in a thermostat at 25°C, and the pH of the solution was measured with a Toa Denpa pH meter, model HM-8, after the equilibrium had been established.

Results

The Determination of the Acid Dissociation Constants of Glycine and α-Alanine.—It is reasonable to presume that α-amino acids are present in an aqueous solution in the three species as H_3N^+—CHR—COOH, H_3N^+—CHR—COO^- and H_2N—CHR—COO^-, where R is H for glycine and R is CH_3 for α-alanine.

When these three species are expressed by H_2A^+, HA and A^- respectively, the acid dissociation constants of the amino acid are defined as follows:

$$H_2A^+ \rightleftarrows H^+ + HA \quad K_1=[H^+][HA]/[H_2A^+] \quad (1)$$

$$HA \rightleftarrows H^+ + A^- \quad K_2=[H^+][A^-]/[HA] \quad (2)$$

where [ ] expresses the concentration of each species in mole per liter.

The acid dissociation constants of glycine at 0.1 of ionic strength and at 25°C were taken from a preceding work[3] to be $pK_1=2.43$ and $pK_2=9.62$, but those of α-alanine have never been known. They were determined by titrating the aqueous solution at an ionic strength of 0.1 and at 25°C with hydrochloric acid or sodium hydroxide and by applying the following equation[3]:

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

or

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

where C is the total concentration of amino acid, and A and B are the concentrations of hydrochloric acid and sodium hydroxide solution as calculated from their titres. The values of $[H^+]$ and $[OH^-]$ were calculated by applying the activity coefficient of hydrogen ion at an ionic strength of 0.1 to the activity of the hydrogen ion obtained by pH measurement. The results of titration with hydrochloric acid are listed in Table I, those with sodium hydroxide being, however, omitted. The acid dissociation constants of α-alanine have been found to be $pK_1=2.53$ and $pK_2=9.59$ respectively.

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

Table I. Determination of acid dissociation constants, pK_1

Concentration of HCl: 0.10403 N
Initial concentration of α-alanine: 0.01 mol./l.
$\mu=0.1$, 25°C

Titre of HCl, ml.	pH	$[H^+]\times10^4$	$A\times10^4$	pK_1
0.1	4.37	0.5139	2.076	2.49
0.2	4.04	1.099	4.351	2.49
0.3	3.88	1.588	6.205	2.49
0.4	3.76	2.094	8.256	2.50
0.5	3.66	2.636	10.30	2.50
0.6	3.58	3.169	12.34	2.51
0.7	3.51	3.724	14.36	2.51
0.8	3.45	4.275	16.38	2.51
0.9	3.39	4.908	18.39	2.51
1.0	3.35	5.381	20.40	2.53
1.1	3.31	5.900	22.39	2.54
1.2	3.27	6.470	24.38	2.54
1.3	3.23	7.095	26.36	2.54
1.4	3.19	7.779	28.34	2.54
1.5	3.16	8.335	30.30	2.54
1.6	3.13	8.930	32.26	2.55
1.7	3.10	9.570	34.21	2.55
1.8	3.07	10.26	36.15	2.55
1.9	3.05	10.74	38.08	2.57
2.0	3.02	11.51	40.01	2.56
			mean	2.53

The Determination of the Formation Constants of Glycinato and α-Alaninato Chromium(III) Complexes.—When the total concentrations of chromium, of amino acid as a ligand and of the total ionizable hydrogen, including $HClO_4$, are expressed by C_M, C_A and C_H respectively, the following relationships exist:

$$C_A = [A^-] + [HA] + [H_2A^+] + \bar{n}C_M \quad (3)$$

$$C_H = [H^+] + [HA] + 2[H_2A^+] \quad (4)$$

where $\bar{n}$ is the average number of ligands attached to each chromium ion.

The value of n is calculated by the following equation, on the basis of Eqs. 3 and 4:

$$\bar{n}=\left\{C_A-\frac{C_H-[H^+]}{\bar{n}_H}\right\}/C_M \quad (5)$$

where $\bar{n}_H$ denotes the number of hydrogen atoms attached to amino acid against the number of the amino acid which does not coordinate to chromium. $\bar{n}_H$ is expressed by using the values of the acid dissociation constants, 1 and 2, such as:

$$\bar{n}_H=\{K_1+2[H^+]\}/\{K_1K_2/[H^+]+K_1+[H^+]\} \quad (6)$$

On the other hand, if the concentrations of

the free perchloric acid contained in the hexaaquochromium(III) perchlorate used as the starting material and of the sodium hydroxide added to the solution are expressed by C_a and C_{OH} respectively, the concentration of the total ionizable hydrogen is given as;

$$C_H = C_a - C_{OH} + C_A \quad (7)$$

By introducing the measured values of the acid dissociation constants and $[H^+]$ values into Eqs. 5, 6 and 7, the values of $\bar{n}$ and $p[A^-]$ were calculated; Table II lists them only for the glycinato chromium(III) complex, those for the α-alaninato complex being omitted. The plots of $\bar{n}$ vs. $p[A^-]$ with relation to glycinato and α-alaninato chromium(III) complexes are shown in Fig. 1. The approximate values of the formation constants of glycinato and α-alaninato chromium(III) complexes were found from the values of the abscissa at $\bar{n}=0.5$ and 1.5 in the formation curves in Fig. 1. The slope of the formation curves was not so steep that the correct values of the formation constants were obtained as $\log K_1=8.62$ and $\log K_2=7.65$ for the glycinato chromium(III) complexes and as $\log K_1=8.53$ and $\log K_2=7.44$ for the α-alaninato chromium(III) complexes by applying the method of successive approximation to the approximate values obtained above.

Table II. The values of $\bar{n}$ and $p[A^-]$ calculated for glycinato chromium(III) complex at $\mu=0.1$ and 25°C

$C_M\times10^3$	$C_A\times10^2$	pH	$\bar{n}$	$p[A^-]$
2.469	0.25	3.89	2.065	6.440
2.469	0.20	3.80	1.995	6.632
2.469	0.15	3.68	1.854	6.887
1.975	0.10	3.72	1.810	7.020
2.469	0.10	3.51	1.715	7.251
1.967	7.50	3.50	1.626	7.387
1.317	0.05	3.63	1.607	7.420
1.967	6.25	3.43	1.511	7.545
1.967	5.00	3.38	1.380	7.685
1.975	0.05	3.45	1.360	7.630
1.967	4.50	3.32	1.230	7.814
1.967	4.00	3.29	1.134	7.901
1.967	3.50	3.25	0.969	8.004
1.967	3.04	3.20	0.860	8.125
0.983	1.20	3.21	0.651	8.510
3.950	0.025	3.00	0.527	8.780
0.983	0.80	3.11	0.513	8.810
0.983	0.60	3.06	0.359	9.010
0.983	0.40	2.98	0.278	9.260
0.983	0.20	2.90	0.125	9.720

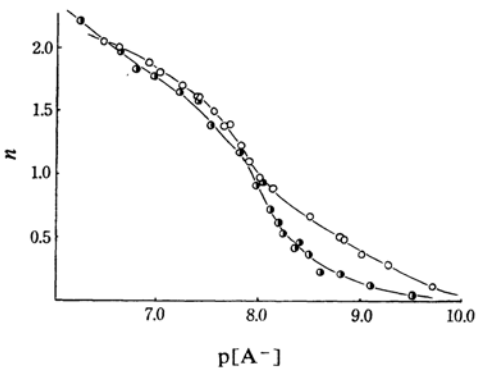


Fig. 1. The formation curve, $\bar{n}$-$p[A^-]$.
○ Chromium(III) glycinato complexes
◑ Chromium(III) α-alaninato complexes

Discussion

The values of the formation constants of chromium(III) glycinato and α-alaninato complexes obtained in the present study are summarized in Table III, together with those of chromium(III) ethylenediamine and oxalato complexes reported by the present authors in preceding papers.[1,2]

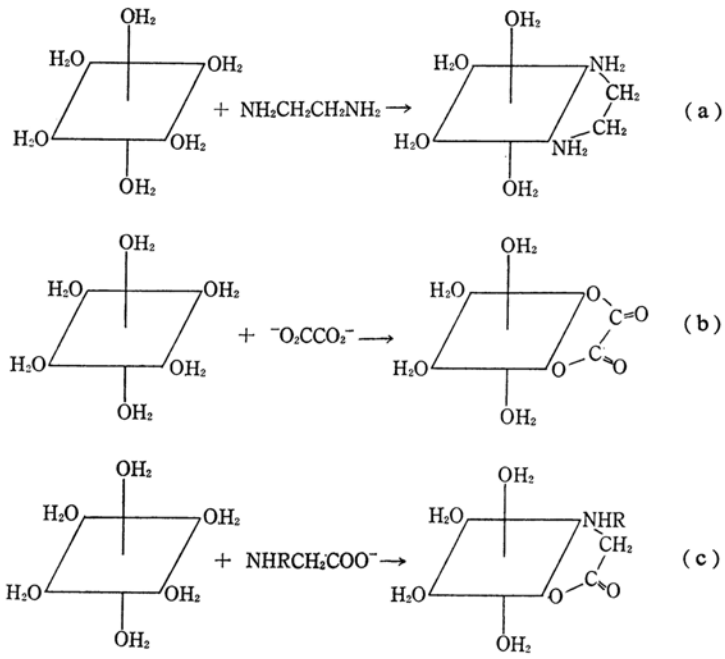
This table indicates, first, that the formation constants of glycinato and α-alaninato complexs are nearly all the same. This may be due to the fact that these two amino acids form the same five-membered chelate ring with chromium ions except that α-alanine has a methyl group, whereas glycine has none. It may also be suggested that the presence of a methyl group in the side chain of α-amino acids has little influence upon the ability to form chromium(III) complexes.

Table III also shows that the values of the formation constants of glycinato and α-alaninato complexes are between those of ethylenediamine and oxalato complexes. This is to be expected from the fact that glycine and α-alanine are N, O-type ligands, whereas ethylenediamine is an N, N-type ligand and the oxalate ion is an O, O-type ligand.

Table III. The formation constants of ethylenediamine-, glycinato-, α-alaninato-, and oxalato-chromium(III) complexes in aqueous solution of ionic strength 0.1 at 25°C

	$\log k_1$	$\log k_2$
Ethylenediamine complex	16.5	<14
Glycinato complex	8.62	7.65
α-Alaninato complex	8.53	7.44
Oxalato complex	5.34	5.17

When the values in Table III are compared with each other in more detail, it is found that the values of the formation constants of glycinato and α-alaninato complexes are closer to those of oxalato complexes rather than to those of ethylenediamine complexes. Although



it is impossible to account this fact completely satisfactorily, it may be roughly understood in terms of speculation concerning the entropy effect.

Let us take into account the processes by which mono-ethylenediamine, mono-oxalato and mono-α-amino acid complexes are formed from the hexaaquo complex by the following processes, a, b and c:

The free energies of formation in the processes, a, b and c, are expressed by the enthalpy and entropy terms as follows:

$$\Delta G_{en} = \Delta H_{en} - T\Delta S_{en} \quad (8)$$

$$\Delta G_{ox} = \Delta H_{ox} - T\Delta S_{ox} \quad (9)$$

$$\Delta G_{a} = \Delta H_{a} - T\Delta S_{a} \quad (10)$$

where the suffixes en, ox and a designate the processes a, b and c. If it is crudely assumed that the bond energy of chromium with α-amino acid as the N, O-type ligand is approximately equal to the mean value of the bond energy of chromium with ethylenediamine as an N, N-type ligand and that of the chromium with the oxalate ion as an O, O-type ligand, then the following equation may be roughly presented:

$$\Delta H_{a} \fallingdotseq 1/2\ (\Delta H_{en} + \Delta H_{ox}) \quad (11)$$

By substracting Eq. 10 from half of the sum of Eqs. 8 and 9 and by taking Eq. 11 into account, the following equation is obtained:

$$\Delta G_{a} - 1/2(G_{en} + \Delta G_{ox}) = T\left(\frac{\Delta S_{en} + \Delta S_{ox}}{2} - \Delta S_{a}\right) \quad (12)$$

As the rough values of the free energies of the formation of ethylenediamine, oxalato and glycinato complexes in the processes a, b and c, $\Delta G_{en} = -27$ kcal., $\Delta G_{ox} = -9$ kcal. and $\Delta G_{a} = -14$ kcal. are, respectively, obtained from the formation constants in Table III. When we insert those values into Eq. 12, we can obtain the difference between the mean values of the entropy changes of the formation of ethylenediamine in the process a and of oxalato complexes in b and the value of the entropy change of the formation of the glycinato complex in c. If the entropy changes of the formation of ethylenediamine and oxalato complexes are assumed to be approximately equal because of the resemblance between their changes in atomic configuration, the rough relation below is obtained:

$$(-\Delta S_{a}) - (-\Delta S_{en} \text{ or } -S_{ox}) = 14 \text{ e. u.}$$

This shows that the entropy decrease in the formation of the glycinato complex is larger by about 14 entropy units than the entropy decrease in the formation of the ethylenediamine or oxalato complex; this can be roughly understood by considering that mono-ethylenediamine and mono-oxalato complexes have roughly a symmetry such as C_{2v}, whereas the mono-α-amino acid complexes have a lower symmetry such as C_s.

Summary

The formation constants of chromium(III) glycinato and α-alaninato complexes have been

determined by the pH method. The values connected with these two complexes are so close to each other that no effect of the presence of a methyl group could be found.

The values of the first formation constants of these complexes are smaller than the mean value of those of ethylenediamine and oxalato complexes. These facts have been explained in terms of the finding that the decrease in the entropies of the formation of α-amino acid complexes is larger than that of ethylenediamine or oxalato complexes because the symmetry of the amino acid complexes is lower than that of the ethylenediamine or oxalato complexes.

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