BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 397—400 (1970)

Chromium(III) Complexes with Iminodiacetic Acid or *l*-Aspartic Acid[*1]

Hisayuki MIZUOCHI,[*2] Shuichi SHIRAKATA, Eishin KYUNO and Ryokichi TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

(Received July 29, 1969)

The formation constants of chromium(III) complexes with iminodiacetic acid (IDA) and *l*-aspartic acid (Asp) as the terdentate ligands were determined by the pH method in the ionic strength, $\mu=0.1$ and at 25°C: their values were $\log k_1=10.9$ and $\log k_2=10.5$ for IDA and $\log k_1=10.1$ and $\log k_2=9.5$ for Asp, respectively. That the overall formation constants of chromium(III)-IDA complexes obtained were slightly larger than those of the corresponding -Asp complexes was explained by the stronger chelate effect in the former complexes than in the latter ones. The solid chromium(III) complexes with IDA and Asp were also prepared. Based on chemical analyses and the conductivity measurement or the behavior toward the ion exchangers, the chemical formulas of these complexes are possibly $K[Cr(ida)_2]\cdot 3H_2O$ and $K[Cr(OH)_2asp]$ respectively. X-Ray powder diffraction patterns indicated that the former crystalline complex has tetragonal unit lattice, the axial parameter being $a=14.57$ and $c=12.38$ Å, whereas the latter is amorphous solid.

The formation constants of chromium(III) complexes with glycine and α-alanine as the natural amino acids,[1] anthranilic acid, picolinic acid and 8-hydroxyquinoline,[2] behaving as the (N,O)-type, bidentate ligands, have already been determined. In the series of studies on the formation constants of chromium(III) complexes, the iminodiacetic acid (abbreviated as IDA) and *l*-aspartic acid (abbreviated as Asp) were selected as the (N,O,O)-type, terdentate chelate ligands. We intend first to determine the formation constants of chromium(III) complexes with IDA and Asp in order to compare their stability with that of glycine and to discuss the difference between them.

A series of the systematic syntheses of the chromium(III) complexes containing diamines and dicarboxylic acids as mixed ligands has been investigated.[3] The complexes with nitrilotriacetic acid and its homologues as the artificial amino acids which can behave as quadridentate ligands were synthesized, and their coordinating structures have been discussed.[4] However, no details of the comparative syntheses of chromium(III) complexes with the amino acids which can behave as the terdentate chelate ligands are known. The second purpose of this study is to prepare chromium(III) complexes with IDA and Asp in the solid phase.

[*1] Read at the 19th Annual Meeting and at the 16th Symposium on Coordination Compounds of the Chemical Society of Japan, Tokyo, April and December, respectively, 1966.

[*2] Present address: Yamanouchi Rubber Industries Co. Ltd., Hirakata, Osaka.

1) H. Matsukawa, M. Ohta, S. Takata and R. Tsuchiya, This Bulletin, **38**, 1235 (1965).

2) S. Takata, E. Kyuno and R. Tsuchiya, *ibid.*, **41**, 2416 (1968).

3) E. Kyuno, M. Kamada and N. Tanaka, *ibid.*, **40**, 1848 (1967).

4) A. Uehara, E. Kyuno and R. Tsuchiya, *ibid.*, **40**, 2317, 2322 (1967); **41**, 2385, 2393 (1968).

Experimental

Materials. The stock solution of hexaaquochromium(III) perchlorate for the measurement of the formation constants was prepared as described in a previous paper.[1] IDA as a chelating agent used was of highest commercial grade supplied by Dojin Institute of Pharmaceutical Chemistry, and Asp was of special grade by Wako Pure Chemical Industries, Ltd.

Formation Constant Measurements. The formation constants of chromium(III)-IDA and -Asp complexes were determined by the pH method as described.[1] The pH value was measured with a Toa Denpa pH meter, model HM-8. The pH value decreased very slowly as the complex formation proceeds in the mixed solution of hexaaquochromium(III) perchlorate and IDA or Asp, owing to the inertness of chromium(III) complexes. When the decrease of the pH values ceased and the value remained constant for one or one-and-half months, the equilibrium of the complex formation reaction was presumed to be attained. It was also checked by the invariance of the optical density of the reaction solution. In order to see whether some effects upon the pH value due to the unexpected circumstances appear or not, the pH of the solution of the respective chelating agent alone, in the absence of hexaaquochromium(III) perchlorate, was occasionally measured as a blank test for the measurement of the formation constant. It was confirmed that the values remained unchanged during the desired period. Thus, after the pH value of the solution in question became constant, the formation constants were calculated.

Preparation of Complexes. In order to prepare solid chromium(III) complexes with IDA, an aqueous solution of chromium(III) nitrate was mixed with that of IDA in the mole ratio 1 : 3, and then was allowed to boil for a few minutes. After potassium hydroxide was added to the solution to keep the pH value at 3.5—4, it was concentrated to some extent and then ethanol was poured into it. After the solution had been stood for a while, fairly large, red crystals were deposited. If the solution was kept in an ice-box, scale-like, red crystals were produced. Results of chemical and thermal analyses of the crystalline chromium(III)-IDA complex obtained above were as follows: Found: Cr, 12.82; K, 9.73; C, 23.56; N, 6.51; H, 3.75; H_2O, 12.42%. Calcd for $K[Cr(ida)_2]\cdot 3H_2O$: Cr, 12.77; K, 9.60; C, 23.59; N, 6.88; H, 3.93; H_2O, 13.27%.

The content of crystalline water was evaluated from the result of the thermogravimetric analysis by a thermobalance.

Synthesis of crystalline chromium(III) complex with *l*-aspartic acid corresponding to that with IDA which has the composition of 1 : 2 mole ratio was unsuccessful. However, another type of complex was prepared at higher pH. About five grams of *l*-aspartic acid in 500 m*l* of water was warmed on the water bath. After it was dissolved, 5 g of chromium(III) nitrate trihydrate was added and the solution was heated for ten minutes. When 20 g of potassium carbonate were gradually added into the solution with stirring, it turned from reddish-violet to bluish-green. As soon as a scale-like film was formed on the surface of the solution, it was filtered while hot. The yield was very poor, 20 mg at most. The result of analysis was as follows: Found: Cr, 20.56; K, 14.22; C, 21.69; H, 2.13%. Calcd for $K[Cr(OH)_2asp]$: Cr, 20.30; K, 15.26; C, 20.09; H, 2.11%.

Other Measurements. Measurements of the conductivity in an aqueous solution, thermogravimetric analysis and X-ray diffraction in the solid state were carried out with a Yokogawa Universal Bridge, BV-Z-13A, a Shimadzu TM-1A type Thermobalance and a Rigaku-Denki Geiger-flex X-ray Analyzer, respectively.

Results and Discusson

Continuous Variation Method. Prior to determination of the formation constants of the complexes, the continuous variation method was applied to the system of the hexaaquochromium(III) perchlorate and IDA or *l*-aspartic acid. The results obtained by this method at pH 2, and 3—4 are shown in Fig. 1 for IDA complex and in Fig. 2 for *l*-aspartic acid complex, where the increase of the optical density due to the complex formation was plotted against the mole ratio of the ligand to the sum of metal ion and ligand. The optical density of the solution for Cr(III)-IDA system was measured at both the first and second absorption maxima of $[Cr(ida)_2]^-$, 522 mμ and 389 mμ which were reported by Yamasaki and Ito.[5] Those for Cr(III)-Asp system was measured also at the same wavelength since the corresponding absorption maxima of $[Cr(asp)_2]^-$ are close to those of the former complex.

Since the maxima in the curves shown in Fig. 1 are all found to appear in the mole ratio of metal ion

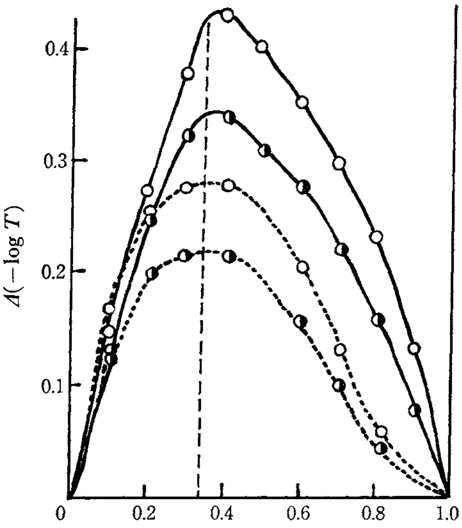


Fig. 1. Continuous variation method for Cr(III)-IDA system.
Full curve: at pH 3—4, Broken curve: at pH 2
○ 522 mμ, ◑ 389 mμ

---

[5] K. Yamasaki and S. Ito, *Proc. Japan Acad.*, **42**, 1077 (1966).

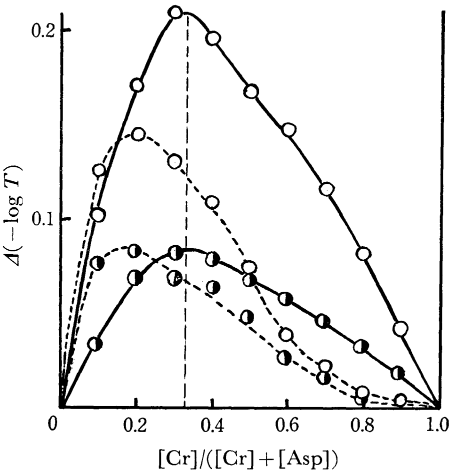


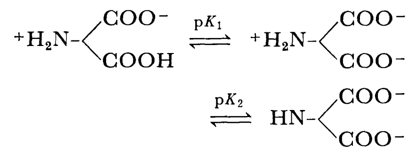
Fig. 2. Continuous variation method for Cr(III)-Asp system.
Full curve: at pH 3—4, Broken curve: at pH 2
○ 522 mμ, ◑ 389 mμ

versus ligand, 1 : 2, the composition of the predominant complex species formed in the solution at pH 2—4 may be $[Cr(ida)_2]^-$. On the other hand, in the case of *l*-aspartic acid complexes as shown in Fig. 2, the maxima in the curves at pH 2 appear in the mole ratio 1 : 3, whereas those at pH 3—4, in the ratio 1 : 2. Hence, the predominant complex species formed may have a composition $[Cr(Hasp)_3]$ at pH 2, and a composition $[Cr(asp)_2]^-$ at pH 3—4.

Conductivity and Behavior toward Ion Exchanger. The results of the molar conductivity of the complex, $K[Cr(ida)_2]\cdot 3H_2O$, in the aqueous solution obtained were 95, 102, 108, 108 and 117 at concentrations of 1/100, 1/250, 1/500, 1/1000 and 1/2000 M, respectively. The complex anion was found to be adsorbed by the anion exchanger, Dowex × 1. It seems that the complex is 1 : 1 valency-type salt and, therefore, the anion is 1 : 2 type complex.

In the solution containing hexaaquochromium(III) perchlorate and *l*-aspartic acid more than three times of chromium(III) salt at pH 2, the complex was found to pass through both cation and anion exchangers, Dowex × 1-Na-form and Dowex × 50-Cl-form, without being adsorbed, but at pH 4, it was adsorbed only by anion exchanger. Therefore, it is presumed that the anionic complex is 1 : 2 type as given by $[Cr(ida)_2]^-$.

Formation Constants. IDA and Asp seem to dissociate in the following manner in an aqueous solution:



$$^{+}H_2N\langle{}^{COO^-}_{COOH} \xrightleftharpoons{pK_1} {}^{+}H_2N\langle{}^{COO^-}_{COO^-} \xrightleftharpoons{pK_2} HN\langle{}^{COO^-}_{COO^-}$$

where all the formulas are expressed only by the functional amino and carboxylate groups without describing the detailed skeleton in each molecule, and K_1 and K_2 are the first and second acid dissociation constants, respectively. In order to determine these values, the aqueous solution of these amino acids in the absence of chromium(III) salt was titrated with the standard solution of sodium hydroxide in the ionic strength $\mu=0.1$ and 25°C. In terms of titration these constants were evaluated by[6)]

$$K_1 = [H^+](aC_A + [H^+])/\{C_A - (aC_A + [H^+])\}$$

in the lower pH range, and by

$$K_2 = [H^+]\{(a-1)C_A - [H^+]\}/[C_A - \{(a-1)C_A - [OH^-]\}]$$

in the higher pH range, where C_A is the total concentration of amino acid, a, the numbers of moles of base added per mole of amino acid present, $[H^+]$ and $[OH^-]$, the concentrations of hydrogen and hydroxide ions respectively. The values for IDA obtained are $pK_1=2.59$ and $pK_2=9.23$. As those for Asp, $pK_1=3.70$ and $pK_2=9.62$ were used from a reference.[7)]

The concentrations of the amino acids non-coordinated to either metal or hydrogen ion, $[A^{2-}]$, and the average number of the ligand coordinated to one mole of metal ion, n were calculated by[6)]

$$[A^{2-}] = \{(2-a)C_A - [H^+] + [OH^-]\}/\{2[H^+]^2/K_1K_2 + [H^+]/K_2\}$$

$$\bar{n} = \{C_A - [H^+]/K_1K_2 + [H^+]/K_2 + 1)[A^{2-}]\}/C_M$$

where C_M is the total concentration of metal.

The formation curves, $\bar{n}$ *vs.* $p[A^{2-}]$, are shown in Fig. 3. By applying the successive approximation method to the values of the stepwise formation constants of chromium(III) complexes with the amino acids found in Fig. 3, the correct values were obtained and are summarized in Table 1 together with those of chromium(III) complexes with glycine.[1)]

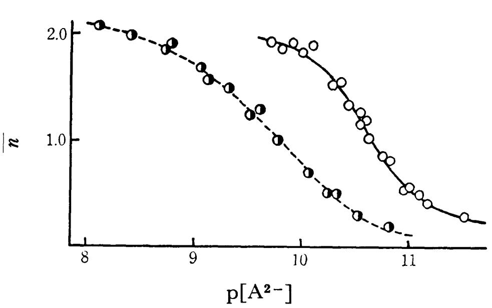


Fig. 3. Formation curve, $\bar{n}$ *vs.* $p[A^{2-}]$ for Cr(III)-IDA (—○—) and Cr(III)-Asp (--◑--) complexes.

[6)] S. Chaberek, Jr., and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 5052 (1952).

[7)] R. F. Lamb and A. E. Martell, *J. Phys. Chem.*, **57**, 690 (1953).

Table 1. Formation constants of chromium(III) complexes with amino acids (μ=0.1, 25°C)

	log k_1	log k_2	log k_3	log β*
Cr(III)-IDA	10.9	10.5	—	21.4
Cr(III)-Asp	10.1	9.5	—	19.6
Cr(III)-Gly	8.62	7.65	5	21.3

* β: overall formation constant

As shown in this table, the formation constants of chromium(III) complexes with IDA are slightly larger than those of the corresponding Asp complexes. This fact can be explained by the difference in the coordinating structures, *viz.*, IDA is a terdentate ligand in the complex, forming two five-membered chelate rings with chromium, where Asp seems to form one five-membered and one six-membered chelate rings as terdentate ligand in the complex.

The overall formation constants of Cr-IDA and Cr-Gly (glycine abbreviated as Gly) complexes are apparently equal to each other. This might be explained as follows.

One IDA complex anion, $[Cr(ida)_2]^-$, contains two IDA molecules coordinating totally with two nitrogen and four oxygen atoms, whereas one glycine complex molecule, $[Cr(gly)_3]$ (gly is the abbreviated form of glycinate anion), contains three glycinate anions coordinating entirely with three nitrogen and three oxygen atoms. If the bond energy of nitrogen with chromium is assumed to be larger than that of oxygen atom, the above glycine complex should be more stable than the IDA complex, so far as the coordinating atoms are concerned.

On the contrary, two molecules of IDA anions form four chelate rings in the $[Cr(ida)_2]^-$ complex, but three glycinate anions form three chelate rings in the $[Cr(gly)_3]$ complex, though their chelate rings formed are all five-membered. A large number of chelate rings in IDA complex than in Gly complex will cause larger entropy change in the former complex formation.

Therefore, the result that the overall formation constants of IDA and Gly complexes are comparable with each other can be explained by the fact that the larger chelate effect in IDA complex is balanced by the stronger bonding force in the latter complex formation.

X-Ray Powder Diffraction Analysis. The results of X-ray powder diffraction analysis for the solid IDA complex, $K[Cr(ida)_2]\cdot 3H_2O$, are listed in Table 2, which shows that it is hexagonal with a tetramolecular unit having the axial parameters a=14.57 Å and c=12.38 Å.

The solid Asp complex, $K[Cr(OH)_2asp]$ was found to be amorphous by X-ray diffraction. When the complex stored over sulfuric acid in a desiccator was exposed to moist air, it gradually began to jump in the same fashion as chromium(III) phthalato[8] and maleato[9] complexes, which was attributed to the absorption of water vapor. The maximum amount of water vapor absorbed by the above chromium(III) aspartato complex was 13.00% for the dried sample. From this value, the solid complex formed by the absorption of water was presumed to have the formula $K[Cr(OH)_2asp]\cdot 2H_2O$, in which the calculated value of the amount of water absorbed is 13.67%.

Table 2. Results of X-ray powder diffraction analyysis

d: lattice distance, *hkl*: Miller's index,
I: intensity

d	*hkl*	*I*	*a*(Å)	*C*(Å)
9.400	011	100	14.51	12.33
7.880	111	20	14.49	12.32
7.308	020	35	14.61	12.42
4.924	030	21	14.77	12.55
4.716	022	20	14.57	12.38
4.530	031	50	14.59	12.40
4.207	131	30	14.19	12.06
3.630	132	12	14.31	12.16
3.437	123	34	14.36	12.21
3.229	240	22	14.44	12.27
2.838	341	22	14.73	12.52
2.805	124	22	14.61	12.42
2.533	243	20	14.43	12.27
1.796	007	18	14.56	12.34
			mean 14.57	mean 12.38

---

[8] K. Higashi, K. Hori and R. Tsuchiya, This Bulletin, **40**, 2569 (1967).

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