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Formation Constants of Chromium(II) Complexes with (O,O)-, (O,N)- and (N,N)-Type Ligands and Comparison with Those of the Other First Transition Metal Complexes[*1]

Yutaka FUKUDA,[*2] Eishin KYUNO and Ryokichi TSUCHIYA

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

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The formation constants of the bivalent chromium complexes with various chelating ligands were determined by the pH titration method at the ionic strength $\mu=0.1$ and at 25°C. The values of the formation constants for (O,O)-type complexes were $\log k_1=3.85\pm0.05$ and $\log k_2=2.96\pm0.05$ for oxalate ion, $\log k_1=3.92\pm0.05$ and $\log k_2=3.21\pm0.05$ for malonate ion, and $\log k_1=9.89\pm0.05$ for sulfosalicylate ion: for (O,N)-type complexes we obtained $\log k_1=7.72\pm0.05$ and $\log k_2=7.54\pm0.05$ for glycine, $\log k_1=9.05\pm0.05$ for 8-hydroxyquinoline, and $\log k_1=7.53\pm0.05$ for β-alanine. Based on these values together with the corresponding values of the (N,N)-type complexes, the effect of the coordinating atoms and of the number of members in a chelate ring upon the stabilities was discussed. These values were compared with those for the other transition metal complexes.

There are many unknown formation constants on the complexes of d^4-type metal ions, such as vanadium(I), chromium(II), manganese(III) and iron(IV). This may be mainly attributed to their variable valencies owing to the easy oxidation to d^3-type electronic state as shown by the standard reduction potential such as $E_{298}{}^0=-0.41$ V[1] for Cr^{2+}–Cr^{3+} system or to the easy reduction to d^5-type state as shown by the standard oxidation potential such as $E_{298}{}^0=1.51$ V[1] for Mn^{2+}–Mn^{3+} system. The corresponding potentials for V^+–V^{2+} and Fe^{3+}–Fe^{4+} are not known. Thus, because of the instability of the bivalent chromium ion in an aqueous solution, the formation constants have not been determined except for a few complexes, such as sulfosalicylic and salicylic acids,[2] acetylacetone,[3] ethylenediamine[4] and α,α'-bipyridyl.[5]

The present work was undertaken (1) to provide enough data on the formation constants of the chromium(II) complexes to find the effect of the coordinating atoms on the stabilities among the (O,O)-, (O,N)- and (N,N)-type complexes, (2) to know the effect of the number of members forming the chelate upon the stabilities and (3) to clarify the position of the chromium(II) complexes in the series of the stability order.

Experimental

Ligand Materials. The (O,O)-type chelating ligands were oxalic, malonic and sulfosalicylic acids, and the (O,N)-type ligands were glycine, 8-hydroxy-

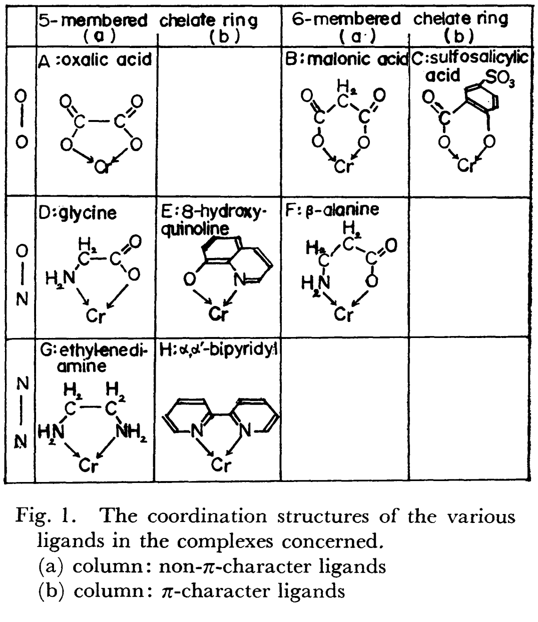

Fig. 1. The coordination structures of the various ligands in the complexes concerned.
(a) column: non-π-character ligands
(b) column: π-character ligands

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[*2] Present address: Department of Chemistry, Faculty of Science, Shizuoka University, Shizuoka.

1) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., Englewood Cliffs, N. J. (1961).

2) R. L. Pecsok and W. P. Schaefer, *J. Amer. Chem. Soc.*, **83**, 62 (1961).

3) W. P. Schaefer and M. E. Mathisen, *Inorg. Chem.*, **4**, 431 (1965).

4) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

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quinoline and β-alanine. They were all of special grade reagents from Wako Pure Chemical Industries. For the sake of convenience, the structures of the ligands are given in Fig. 1.

Preparation of Chromium(II) Perchlorate. A solution of chromium(II) perchlorate was prepared by the electrolytic reduction of a solution of hexaaquochromium(III) perchlorate.6) The cell for electrolysis consists of three compartments:2) in one compartment the so-called Winkler platinum electrode was inserted as an anode and in another one mercury was used as a cathode. The starting voltage was 2—3 V in the electrolysis. The applied voltage was gradually raised to about 6 V, keeping the electric current at about 0.5 A. Electrolysis was continued under these conditions for 7—8 hr, nitrogen being passed through all the apparatus not only during the electrolysis but also for 2—3 hr before the electrolysis to protect the bivalent chromium ion from oxidation. Nitrogen was purified by passing it through a basic pyrogallol solution and a chromium(II) ion solution.

The color of the electrolytic solution changed from reddish-violet to blue as the reduction proceeded. The absorption spectrum of the resulting solution in a *d-d* transition region was found to coincide with that of aquo chromium(II) complex.7) Determination of the chromium(II) ion content was carried out iodometrically: a standard solution of potassium iodate, in the presence of potassium iodide and a few drops of starch solution as indicator, was titrated with the chromium(II) perchlorate solution prepared by electrolytic reduction, and the concentration of chromium(II) ion was calculated from the titres. The reactions concerned can be expressed by the following:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$3I_2 + 6Cr^{2+} \rightarrow 6I^- + 6Cr^{3+}$$

Total concentration of chromium was spectrophotometrically determined as bichromate. Although the accuracy of the determination of total chromium content is about ten times less than that of the chromium(II) content evaluated from the iodometric titration, it could be confirmed by this procedure that more than 99% of the chromium was reduced.

Formation Constant Measurement. The aqueous solution of each ligand was titrated with alkali hydroxide solution at an ionic strength $\mu=0.1$ and at 25°C, in the presence as well as in the absence of the hexaaquochromium(II) perchlorate. The ligand materials were used in excess in comparison to the chromium(II) perchlorate added. Thus the change of the concentration of the ligands in complex formation can be neglected as compared with the total concentration of the ligands added. The ionic strength of the solution was adjusted to 0.1 by adding an appropriate amount of sodium perchlorate.

Results

When the ligand materials behave as bidentate chelating agents, the acid dissociation constants[*3] are given by

$$H_2L = H^+ + HL, \quad K_1 = [H^+][HL]/[H_2L],$$
$$HL = H^+ + L, \quad K_2 = [H^+][L]/[HL],$$

where the square brackets, [ ], express the concentration of relevant species, and the ionic charges are omitted except for hydrogen ion. From the equations, the concentration of the free ligand bound neither with proton nor with metal ions, [L], is calculated by the equation:

$$[L] = K_1K_2[C_L]/\{K_1K_2 + K_1[H^+] + [H^+]^2\}, \qquad (1)$$

where $[C_L]$ is the total concentration of the ligand.

The average number of the coordinated ligands per one chromium(II) ion, $\bar{n}$, is expressed by the equation

$$\bar{n} = C_{OH}[OH^-]/2C_M V_M, \qquad (2)$$

where C_{OH} and C_M are the initial concentrations of alkali hydroxide and chromium(II) perchlorate solution, respectively, V_M is the titres of the chromium(II) perchlorate solution and $[OH^-]$ is the difference between the titres obtained from pH titration curves in the presence and absence of the metal ion at the same pH value of the solution. $[OH^-]$ corresponds to the amount of the ligand participating in the complex formation.8)

The values, $\bar{n}$ and the logarithm of the reciprocal concentration of the free ligand, p[L], are calculated by using equations, (1) and (2). The formation curves, $\bar{n}$—p[L], are plotted in Fig. 2.

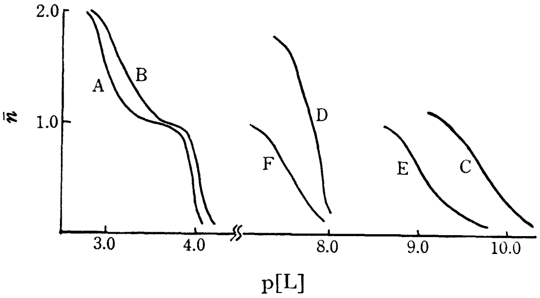

Fig. 2. The formation curves, $\bar{n}$—p[L], for chromium(II)-various ligands systems.
A: oxalic acid, B: malonic acid, C: sulfosalicylic acid, D: glycine, E: 8-hydroxyquinoline, F: β-alanine.

The values of the formation constants of the chromium(II) complexes obtained from Fig. 2 were refined by means of successive approximation. The final values are summarized in Table 1, together with those for salicylic and sulfosalicylic acids,2) acetylacetone,3) ethylenediamine,4) and α,α′-bi-

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6) H. Matsukawa, M. Ohta, S. Takata and R. Tsuchiya, This Bulletin, **38**, 1235 (1964).

7) J. P. Fackler, Jr., and D. G. Halah, *Inorg. Chem.*, **4**, 954 (1965).

[*3] The values of the acid dissociation constants are cited from literature, and are given in Table 1.

8) M. Calvin and N. C. Melchoir, *J. Amer. Chem. Soc.*, **70**, 3270 (1948).

pyridyl.[5] In Table 1 are also included the acid dissociation constants of the relevant ligands.

TABLE 1. FORMATION CONSTANTS OF THE CHROMIUM(II) COMPLEXES WITH VARIOUS CHELATE LIDANDS, AND THE ACID DISSOCIATION CONSTANTS OF THE LIGANDS

Coordination ligand type	log k_1	log k_2	pK_1	pK_2
(A)	3.85±0.05	2.96±0.05	1.37	3.81[9]
(B)	3.92±0.05	3.21±0.05	2.76	5.29[10]
(C)	9.89±0.05	—	2.62	11.95[11]
	7.14	5.74[2]		
(I)*	5.96	5.74[3]	8.88[3]	
(J)*	8.41	6.95[2]	3.18	13.12[2]
(D)	7.72±0.05	7.54±0.05	2.35	9.68[12]
(E)	9.05±0.05	—	3.97	11.54[13]
(F)	7.53±0.05	—	3.52	10.26[14]
(G)	5.15	4.04[4]	7.44	10.06[4]
(H)	4	6.4[5]	4.44[5]	

* I: acetylacetone, J: salicylic acid

Discussion

Comparison of the Formation Constants. It may be deduced from Fig. 2 that the chromium(II) complexes having two ligand molecules at highest appear in aqueous solution. This may be due to the so-called Jahn-Teller effect in d^4-type complexes, the electronic configuration preferring the high-spin state.

The 1 : 3 complex was found only in α,α′-bipyridyl in an aqueous solution.[5] It was also confirmed by preliminary experiment that the yellow crystalline tervalent chromium complex with α,α′-bipyridyl was obtained by oxidizing the crystalline black chromium(II) complex prepared in nitrogen atmosphere in the air. The fact that chromium(II) forms 1 : 3 complex only with α,α′-bipyridyl may suggest that only the complex with α,α′-bipyridyl is in the low-spin state.

In the case of chromium(III) complexes, the stability is known to increase, in general, in the order of the ligands giving the coordination types, *viz.*, (O,O)<(O,N)<(N,N).[6] This may be due to the fact that the polarizing ability of the chromium(III) ion is relatively stronger owing to its greater ionic charge and smaller ionic radius than that of the chromium(II) ion and that the polarizability of nitrogen as a soft base[15] is larger than that of oxygen.

In chromium(II) complexes, the following results are given in Fig. 2 and Table 1. For the ligands forming five-membered chelate ring with metal, the formation constants of the (O,N)-type complexes such as glycinate and 8-hydroxyquinolinate are larger than those of the (O,O)-type complexes such as oxalate. This is in line with the results obtained with the chromium(III) complexes.[6] The same stability order applies also to the ligands forming six-membered chelate ring: the formation constants of the (O,N)-type complexes such as β-alaninate are larger than those of the (O,O)-type complexes such as malonate or acetylacetonate.

The formation constants of the (N,N)-type complexes such as ethylenediamine and α,α′-bipyridyl are slightly larger than those of the (O,O)-type complexes such as oxalate or malonate. This may be explained as above with respect to the corresponding chromium(III) complexes: the strength as Lewis base is larger in nitrogen than in oxygen atoms, or nitrogen is a more soft base than oxygen.[9]

However, the formation constants of chromium(II) complexes with ethylenediamine and α,α′-bipyridyl are, contrary to expectation, smaller than those of the (O,N)-type complexes such as glycinate and 8-hydroxyquinolinate. This fact was not found with the chromium(III) complexes reported in an earlier paper.[6]

It is known that the complexes having five-membered chelate ring are, in general, more stable than those having six-membered chelate ring. Nevertheless, so far as chromium(II) complexes are concerned, the difference is not appreciable between the formation constants of complexes forming five-membered and those forming six-membered chelate rings as seen in the (O,O)-type complexes such as oxalate and malonate or in the (O,N)-type complexes such as glycinate and β-alaninate.

The salicylate and sulfosalicylate complexes, however, have exceptionally larger formation constants than those of malonate complexes having the same six-membered chelate ring of (O,O)-type. 8-Hydroxyquinolinate complex has a larger value of the formation constants than that of glycinate complex having the same five-membered ring of (O,N)-type. Salicylic and sulfosalicylic acids have benzene ring, and 8-hydroxyquinoline has a pyridine ring besides a benzene ring. The reason why the complexes containing such chelating ligands are extraordinarily stable comes from the possibility of the resonance effect resulting from the presence of a

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9) A. McAulley and G. H. Nancollas, *Trans. Faraday Soc.*, **56**, 1165 (1960).

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

11) D. D. Perrin, *Nature*, **182**, 741 (1958).

12) N. C. Li and R. A. Manning, *J. Amer. Chem. Soc.*, **77**, 5225 (1955).

13) W. D. Johnston and H. Freiser, *ibid.*, **74**, 5239 (1952).

14) H. Irving, R. J. P. Williams, D. J. Ferrett and A. E. Williams, *J. Chem. Soc.*, **1954**, 3494.

15) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

benzene or pyridine ring and/or the change of the electronic configuration in chromium(II) ion from the high-spin to the low-spin state.

In the case of α,α'-bipyridyl complexes, the second stepwise formation constant is larger than the first one as shown by their data.[5] The normal order where the first stepwise formation constant is larger than the second one as seen in most complexes is not applied to the case of α,α'-bipyridyl complexes. Such an abnormal result suggests that the electronic configuration in these complexes may be changed from the high-spin to the low-spin state when the 1 : 1 complex is converted to 1 : 2 complex.

The fact that the acetylacetonate complexes have larger values of formation constants than the malonate ones which have the same six-membered ring as seen in Table 1 may be explained by considering the presence of the quasi-aromaticity in the former.

Comparing the formation constants of chromium(II) complexes with the corresponding acid dissociation constants, we see that, when the latter becomes larger, the former tends to increase. The linear relationships between the logarithmic values of the formation constants and of the respective acid dissociation constants are verified by the approximately constant values of $(\log k_1)/\mathrm{p}K_2$ except for oxalate, ethylenediamine and α,α'-bipyridyl complexes. Calculated values are listed in Table 2.

TABLE 2. THE VALUES OF $(\log k_1)/\mathrm{p}K_2$

Complex	$(\log k_1)/\mathrm{p}K_2$
A	1.01
B	0.74
C	0.83
I	0.66
J	0.64
D	0.80
E	0.78
F	0.73
G	0.51
H	0.90

Position of the Stability of Chromium(II) Complexes in the First Transition Metal Complexes. So far enough data of the formation constants of the bivalent chromium complexes have not been obtained, and the position of the constants in the so-called Irving-Williams series[16] is ambiguous. In order to survey the stability sequence in various complexes of the first bivalent transition metal, ion formation constants of some chelates of these metals ion are plotted against the metal series following their atomic numbers in Fig. 3.

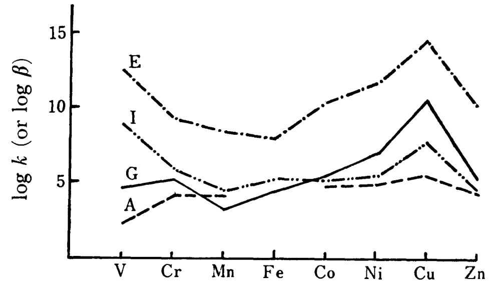

Fig. 3. Comparison of the stabilities of the bivalent metal complexes with various chelate ligands.
E: 8-hydroxyquinoline, I: acetylacetone,
G: ethylenediamine, A: oxalic acid.

A approximate order of the stability of the first transition metal complexes including chromium is found to be $\mathrm{Zn}<\mathrm{Cu}>\mathrm{Ni}>\mathrm{Co}\gtrsim\mathrm{Cr}>\mathrm{Fe}>\mathrm{Mn}$. The stability of chromium(II) complexes seems to be situated between that of iron(II) and cobalt(II) complexes, so far as the chelating lignads such as 8-hydroxyquinoline and ethylenediamine are concerned.

The order found for cobalt(II), iron(II) and chromium(II) complexes may be explained on the basis of the ligand field theory as follows: if the electronic configuration in these complexes is in the high-spin state as given in Fig. 4, the ligand field stabilization energy can be calculated as $4/5\Delta$, $2/5\Delta$ and $3/5\Delta$ for Co(II), Fe(II) and Cr(II) complexes, respectively, in octahedral environment, where Δ is the splitting energy dependent upon the strength of the ligand field. Since all the values of Δ are not known, the explanation by the ligand field theory is not always applicable to each stability sequence over the first transition metal complexes with various chelating ligands.

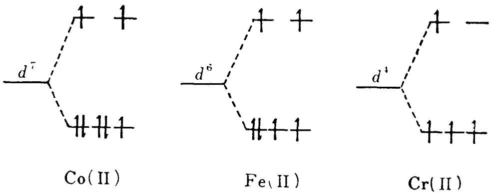

Fig. 4. Ligand field splitting in Co(II), Fe(II) and Cr(II) complexes in high-spin state.

It will be found from Fig. 3 that the stability of the chromium(II) complexes which contain the π-character ligands such as 8-hydroxyquinoline or acetylacetone is lower than that of the corresponding vanadium(II) complexes, whereas, in the case of the complexes containing normal ligands such as oxalic acid or ethylenediamine, their stabilities are in reverse order. The reason might be as follows: since the radius of chromium(II) ion is smaller than that of vanadium(II) ion, the former is a harder acid than the latter, so that the chromium-

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[16] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.

(II) complex is more stable than vanadium(II) for a common chelating ligand having no π-character, whereas the strength of the back-coordination is larger in chromium(II) than in vanadium(II) for a π-character ligand, so that the stability order might become reverse.