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Stability Constants of Cu(II) Chelates with *o*-Phenylenediamine Derivatives

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The stability constants of copper(II) chelates with *o*-phenylenediamine derivatives have been determined by the pH titration method. The measurements have been carried out at 25.0±0.1°C and $\mu=0.10$(by KNO_3). *o*-Phenylenediamine derivatives, which have a substituent group (CH_3, CH_3O, COOH, or Cl, *etc.*) at the 4 positions, were used as ligands. The overall stability constants of the copper chelates are of the order: CH_3, CH_3O, H, COO^-, Cl, COOH; their values were 8.50, 8.42, 7.72, 7.06, 5.76, and 5.35 respectively. The effects of substituent groups on the stability constants have been studied. The plot of the overall stability constants against the sum of Hammett σ_m and σ_p values was found to be linear. The chelate stability and acid dissociation constants of the acido complexes of 3,4-diaminobenzoic acid were determined by the use of an augmented matrix.

Chelate-compound formation between transition metal ions and aliphatic diamines such as ethylenediamine has been extensively studied.[1] However, an aromatic diamine has not yet been widely studied. The present investigation was undertaken in order to determine the stability constants of copper(II) chelates of aromatic diamines, that is, *o*-phenylenediamine and its derivatives. The stability constants were calculated by the method of the least squares. If the acido complexes are present, the calculation will become enormously troublesome. According to Schwarzenbach, some kinds of ionic species can be neglected in a solution with a certain ratio of the ligand to the metal ion. From this point of view, the problem can be simplified; the acid dissociation and stability constants of acido complex were thus determined.

Experimental

Reagents. *m*-Phenylenediamine, *p*-phenylenediamine, 4-methyl-*o*-phenylenediamine (Wako Pure Chemical Co.), *o*-phenylenediamine (Daiichi Pure Chemical Co.), 4-chloro-*o*-phenylenediamine, 1,2,4-triaminobenzene dihydrochloride (Tokyo Chemical Industry Co.), and 3,4-diaminobenzoic acid (Aldrich Chemical Co.) were treated with active carbon and were recrystallized from conc. HCl before use.[2] 4-Methoxy-*o*-phenylenediamine was systhesized by the reduction of 2-nitro-4-methoxyaniline.[3] The dihydrochlorides of *o*-phenylenediamine derivatives, and 1,2,4-triaminobenzene trihydrochloride were obtained as white crystals. The hydrochlorides were used for the titration. A carbonate-free potassium hydroxide solution was prepared by the method of ion exchange and was standardized with potassium hydrogen phthalate titrimetrically.

Reagent Solutions. The stock solution of copper(II) ($Cu(NO_3)_2 \cdot 3H_2O$) was standarized by the usual procedures of chelatometric titration.[4] Solutions of all the ligands were made up with redistilled water just before the titration.

pH Titration Method. The hydrogen-ion concentration was measured by using an HRL-Model P pH meter (made by the Horiba Instruments Inc., Kyoto), with glass and calomel electrodes. Before and after each titration, the pH meter was calibrated with an acetate buffer.[5] The titration was carried out in a jacketed titration cell the volume of which was 100m*l*. For the determination of the dissociation constants of the protonated ligands, 2.5×10^{-3}M solutions of ligand in 0.10M potassium nitrate were used. On the other hand, solutions containing 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, or 10:1 molar ratios of the ligand to the metal ion were used for the determination of the stability constants, while the ionic strength was maintained at approximately 0.10M with potassium nitrate. By circulating water from a constant-temperature bath through the water jacket, the temperature of the solution to be measured was kept at 25.0±0.1°C, and the room temperature, at 25±1°C. A carbon dioxide-free nitrogen atmosphere was maintained above the solution.

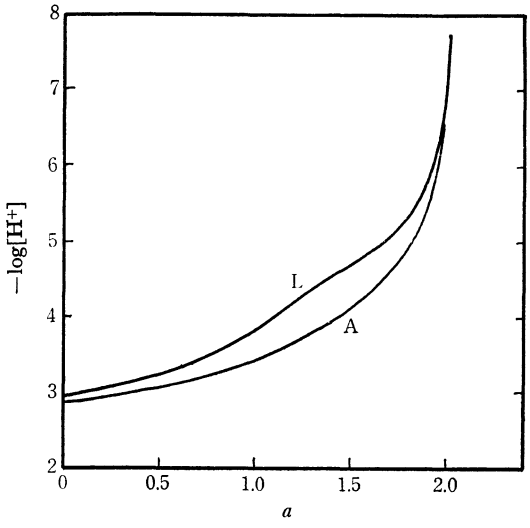

Fig. 1. Titration of *o*-phenylenediamine dihydrochloride, and 2:1 metal chelate, at 25°C, $\mu=0.10$, L, ligand only; A, Cu(II) and ligand mixture [Ligand]=2[Metal ion]=1.052×10^{-3}M, [KOH]=1.072×10^{-3}M, a=moles of base added per mol of ligand.

Mathematical Treatment

a) Acid-dissociation Constants. The acid-dissociation constants of the protonated ligands were calculated

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1) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, Burlington House, London (1964), P. 390.

2) K. Tôei and K. Ito, *Talanta*, **12**, 773 (1965).

3) F. Wrede and E. Strack, *Ber.*, **62**, 2050 (1920).

4) K. Ueno, "Chelatemetric Titration" (in Japanese), Nankodo, Ltd., Tokyo (1967), P. 250.

5) S. Nakashima, H. Miyata, and K. Tôei, This Bulletin, **40**, 870 (1967).

by a method analogous to that of Murakami *et al.*[6] The equilibria and the dissociation constants involved are:

$$\mathrm{H_2L^{2+}} \rightleftharpoons \mathrm{H^+ + HL^+},\quad K_{a1} = [\mathrm{H^+}][\mathrm{HL^+}]/[\mathrm{H_2L^{2+}}],$$

$$\mathrm{HL^+} \rightleftharpoons \mathrm{H^+ + L},\qquad K_{a2} = [\mathrm{H^+}][\mathrm{L}]/[\mathrm{HL^+}],$$

$$1/K_{a1} = \mathrm{A}K_{a2} + \mathrm{B} \tag{1}$$

where:

$$A = (2T_\mathrm{L} - T_\mathrm{OH} - [\mathrm{H^+}] + [\mathrm{OH^-}])/[\mathrm{H^+}]^2(T_\mathrm{OH} + [\mathrm{H^+}] - [\mathrm{OH^-}])$$

$$B = (T_\mathrm{L} - T_\mathrm{OH} - [\mathrm{H^+}] + [\mathrm{OH^-}])/[\mathrm{H^+}](T_\mathrm{OH} + [\mathrm{H^+}] - [\mathrm{OH^-}]),$$

and where L represents the *o*-phenylenediamine or its derivatives. T_L and T_OH are the total ligand concentration, and the concentration of the base added to the system, respectively. In all the calculations, the concentrations were corrected for the change in volume produced by the addition of the KOH. The acid-dissociation constants for protonated ligands were calculated by solving simultaneous equations from two points on the titration curve in the range of the buffer region. The pK_{a2} can be determined accurately by solving the simultaneous equations, because it has an order of magnitude of 3—5. If the pK_{a1} is below 2.0, an accurate value can not be obtained by this method. On the basis of Eq. (1) we assume that pK_{a1} is known and that pK_{a2} is the unknown. Then, pK_{a1} is obtained by the application of iterative approximation, by using an electronic computer (NEAC-2203: Nippon Electric Co., Ltd.).

b) *Stability Constants.* The ligands, 4-chloro, 4-methyl, or 4-methoxy-*o*-phenylenediamine and *o*-phenylenediamine, can have only one proton in the pH 2.8—4.5 region. Such ligands are treated as monoprotic acid in such a region. The equilibria and the stability constants are as follows:

$$\mathrm{M^{2+} + L} \rightleftharpoons \mathrm{ML^{2+}},\quad K_1 = [\mathrm{ML^{2+}}]/[\mathrm{M^{2+}}][\mathrm{L}],$$

$$\mathrm{ML^{2+} + L} \rightleftharpoons \mathrm{ML_2{}^{2+}},\quad K_2 = [\mathrm{ML_2{}^{2+}}]/[\mathrm{ML^{2+}}][\mathrm{L}].$$

The stability constants, K_1 and K_2, were calculated by fitting the data to the Irving and Rossotti equation:[7]

$$\bar{n}/(\bar{n}-1)[\mathrm{L}] = [(2-\bar{n})[\mathrm{L}]/(\bar{n}-1)]K_1K_2 - K_1, \tag{2}$$

which is a linear form.
Here

$$\bar{n} = (T_\mathrm{L} - [\mathrm{L}] - [\mathrm{HL^+}])/T_\mathrm{M},$$

$$[\mathrm{L}] = K_{a2}(2T_\mathrm{L} - T_\mathrm{OH} - [\mathrm{H^+}] + [\mathrm{OH^-}])/[\mathrm{H^+}],$$

$$[\mathrm{HL^+}] = (2T_\mathrm{L} - T_\mathrm{OH} - [\mathrm{H^+}] + [\mathrm{OH^-}]),$$

and T_M is the total metal-ion concentration. The stability constants, K_1 and K_2, are best evaluated by the method of "least squares." The reliability of the constants was verified the theoretical formation curve with the experimental one. Eq. (2) can be rewritten as follows:

$$[\mathrm{L}] = [(1-\bar{n}) - \{(\bar{n}-1)^2K_1{}^2 - 4\bar{n}(\bar{n}-2)K_1K_2\}^{1/2}/K_1]2(\bar{n}-2)K_2. \tag{3}$$

The theoretical formation curves can be generated by the stability constants reported in Table 3 and by Eq. (3).

When the acido complex are present, the acid dissociation and chelate stability constants are obtained by a treatment based on that described by Nagano *et al.*[8] The following equation and equilibria were considered in the 3,4-diamino-benzoic acid system:

$$\begin{tikzcd}
\mathrm{M^{2+}} \arrow[r, shift left, "9)"] \arrow[d, shift right, "K_{\mathrm{M1}}"'] & \mathrm{M(OH)^+} \arrow[l, shift left] \arrow[r, shift left, "10)"] & \mathrm{M(OH)_2} \arrow[l, shift left] \\
\mathrm{MHL^{2+}} \arrow[u, shift right] \arrow[r, shift left, "k_1"] \arrow[d, shift right, "K_{\mathrm{M2}}"'] & \mathrm{ML^+} \arrow[l, shift left] & \\
\mathrm{M(HL)_2{}^{2+}} \arrow[u, shift right] \arrow[r, shift left, "k_2"] & \mathrm{ML(HL)^+} \arrow[l, shift left] \arrow[r, shift left, "k_2'"] & \mathrm{ML_2}. \arrow[l, shift left]
\end{tikzcd}$$

The equilibrium constants are defined as follows:

$$K_\mathrm{M1} = [\mathrm{MHL^{2+}}]/[\mathrm{M^{2+}}][\mathrm{HL}],$$

$$K_\mathrm{M2} = [\mathrm{M(HL)_2{}^{2+}}]/[\mathrm{MHL^{2+}}][\mathrm{HL}],$$

$$k_1 = [\mathrm{H^+}][\mathrm{ML^+}]/[\mathrm{MHL^{2+}}],$$

$$k_2 = [\mathrm{H^+}][\mathrm{ML(HL)^+}]/[\mathrm{M(HL)_2{}^{2+}}],$$

$$k_2' = [\mathrm{H^+}][\mathrm{ML_2}]/[\mathrm{ML(HL)^+}],$$

$$K_{a1} = [\mathrm{H^+}][\mathrm{H_2L^+}]/[\mathrm{H_3L^{2+}}],$$

$$K_{a2} = [\mathrm{H^+}][\mathrm{HL}]/[\mathrm{H_2L^+}],$$

$$K_{a3} = [\mathrm{H^+}][\mathrm{L^-}]/[\mathrm{HL}].$$

The first step of the acid dissociation of protonated ligands is thus complete. As for the total ligand concentration, T_L, the total proton concentration, T_H and the total metal-ion concentration, T_M, the following relations hold:

$$T_\mathrm{L} = \sum_{j=0}^{2}[\mathrm{H}_j\mathrm{L}] + [\mathrm{MHL^{2+}}] + [\mathrm{ML^+}] + 2[\mathrm{M(HL)_2{}^{2+}}] + 2[\mathrm{ML(HL)^+}] + 2[\mathrm{ML_2}] \tag{4}$$

$$T_\mathrm{H} - [\mathrm{H^+}] + [\mathrm{OH^-}] = T_\mathrm{L}\cdot g = \sum_{j=0}^{2} j[\mathrm{H}_j\mathrm{L}] + [\mathrm{MHL^{2+}}] + 2[\mathrm{M(HL)_2{}^{2+}}] + [\mathrm{ML(HL)^+}] \tag{5}$$

$$T_\mathrm{M} = [\mathrm{M^{2+}}] + [\mathrm{MHL^{2+}}] + [\mathrm{ML^+}] + [\mathrm{M(HL)_2{}^{2+}}] + [\mathrm{ML(HL)^+}] + [\mathrm{ML_2}] \tag{6}$$

The average number of hydrogen ions bound per total of the ligands, g, is given by the expressions:

$$g = \sum_{j=1}^{3} j[\mathrm{H}_j\mathrm{L}]/T_\mathrm{L},\quad g = 3 - a + ([\mathrm{OH^-}] - [\mathrm{H^+}])/T_\mathrm{L},$$

a=moles of base added per mole of ligand.
Here a group of brief symbols will be introduced:

$$A = T_\mathrm{L},\ B = T_\mathrm{L}\cdot g,\ C = T_\mathrm{M},\ D_1 = K_\mathrm{M1},\ D_2 = K_\mathrm{M1}k_1,$$

$$D_3 = K_\mathrm{M1}K_\mathrm{M2},\quad D_4 = K_\mathrm{M1}K_\mathrm{M2}k_2,\quad D_5 = K_\mathrm{M1}K_\mathrm{M2}k_2k_2',$$

$$m = [\mathrm{M^{2+}}],\ h = [\mathrm{HL}],\ a_0 = (K_{a3}/[\mathrm{H^+}] + 1 + [\mathrm{H^+}]/K_{a2}),$$

$$b_0 = (1 + 2[\mathrm{H^+}]/K_{a2}).$$

Equations (5), (6), and (7) may be rewritten as follows:

$$A = h\{a_0 + (D_1 + D_2/[\mathrm{H^+}])m + (2D_3 + 2D_4/[\mathrm{H^+}] + 2D_5/[\mathrm{H^+}]^2)mh\} \tag{7}$$

$$B = h\{b_0 + D_1m + (2D_3 + D_4/[\mathrm{H^+}])mh\} \tag{8}$$

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6) Y. Murakami, K. Nakamura, and M. Tokunaga, This Bulletin, **36**, 669 (1963).

7) H. Irving and H. S. Rossotti, *J. Chem. Soc.*, **1953**, 3397.

8) K. Nagano, H. Kinoshita, and Z. Tamura, *Chem. Pharm. Bull.* **11**, 999 (1963).

9), 10) The hydroxo complexes were not taken into consideration, because the equilibria were investigated between pH 2.5 and 5.0.

$$C = m\{1 + (D_1+D_2/[\mathrm{H}^+])h + (D_3+D_4/[\mathrm{H}^+] + D_5/[\mathrm{H}^+]^2)h^2\}. \qquad (9)$$

The elemination of h and m from three independent equations, (7), (8), and (9) will lead to one equation, into which the observed values of five points on the titration curves may be substituted; if the simultaneous equations are solved, all constants can, in principle, be obtained. However, their solution is, in practice, enormously troublesome. This difficulty was overcome by selecting suitable experimental conditions and by iterative approximation using the electronic computer.

1) *Metal-ion-excess Solution.* In this case, the concentration of the free neutral ligand, h, is very small, and only 1:1 species can be present. Equations. (7), (8), and (9) then become:

$$A = h\{a_0 + (D_1+D_2/[\mathrm{H}^+])m\} \qquad (10)$$

$$B = h(b_0+D_1m) \qquad (11)$$

$$C = m\{1 + (D_1+D_2/[\mathrm{H}^+])h\}. \qquad (12)$$

The elimination of the h from (10) and (11) will lead to Eq. (13), $D_1=\{(b_0-ga_0)/m(g-1)\}-\{gD_2/[\mathrm{H}^+](g-1)\}$. Assuming that m is approximately equal to the total metal concentration, and solving simultaneous equations from two points on the titration curve, a first approximation of D_1 and D_2 can be obtained; their temporary constants and m are then substituted into Eq. (10), from which a reasonable value of h is obtained. By the use of these h, D_1, and D_2 values, a more reasonable value of m can be calculated by Eq. (12). This value of m is substituted into Eq. (13), and more reasonable values of D_1 and D_2 are obtained by solving simultaneous equations from two points on the titration curve. This procedure is repeated until the values of these constants converge.

2) *Ligand-excess Solution.* Here, D_1 and D_2 have already been determined from the above solution. In this condition, three chelates, $\mathrm{M(HL)_2}^{2+}$, $\mathrm{ML(HL)}^+$, and $\mathrm{ML_2}$, are present. The elimination of the m from Eqs. (7), (8), and (9) will lead to Eq. (14):

$$l_3D_3 + l_4D_4 + l_5D_5 = L \qquad (14)$$

where;

$$l_3 = (Cf_3-Fh)h,$$
$$l_4 = (Cf_4-F[\mathrm{H}^+]^{-1}h)h,$$
$$l_5 = (Cf_5-F[\mathrm{H}^+]^{-2}h)h,$$
$$L = F\{1 + (D_1+D_2/[\mathrm{H}^+])h\} - C(f_1D_1-f_2D_2),$$
$$f_1 = (g-1),\ f_2 = g[\mathrm{H}^+]^{-1},\ f_3 = 2f_1,\ f_4 = (2g-1)[\mathrm{H}^+]^{-1},$$
$$f_5 = 2g[\mathrm{H}^+]^{-2},\quad b_0 - ga_0 = F.$$

As l_3, l_4, l_5, and L are entirely of known or measurable quantities, D_3, D_4, and D_5 can be obtained by solving simultaneous equations. For the treatment of Eq. (14), a matrix representation is extremely useful. The augmented matrix is:

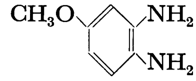
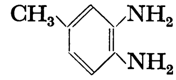
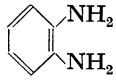
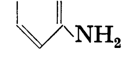
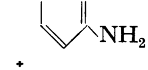
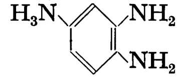
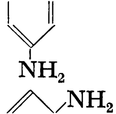
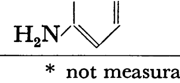
$$\begin{bmatrix} l_{31} & l_{41} & l_{51} & L_1 \\ l_{32} & l_{42} & l_{52} & L_2 \\ l_{33} & l_{43} & l_{53} & L_3 \end{bmatrix} \qquad (15)$$

which is solved by the method of Gauss-Jordan.

Results and Discussion

Acid-dissociation Constants. The acid-dissociation constants of protonated *o*-phenylenediamine derivative were calculated from the titration curve; they are summarized in Table 1. An example of the titration curve is given in Fig. 1. The first step of the acid dissociation of protonated *o*-phenylenediamine derivatives is very

TABLE 1. ACID DISSOCIATION CONSTANTS OF PROTONATED *o*-PHENYLENEDIAMINE DERIVATIVES

Ligand	$\mathrm{p}K_{a1}$	$\mathrm{p}K_{a2}$	$\mathrm{p}K_{a3}$	σ_m[a)]	σ_p[a)]	$\sigma_m+\sigma_p$
	*	5.10		+0.115	−0.268	−0.153
	*	4.79		−0.069	−0.170	−0.239
	*	4.63		0.000	0.000	0.000
	*	3.69	4.75	−0.45	−0.37	+0.82
	(0.6)	3.94		+0.373	+0.227	+0.600
	(1.2)	3.20	5.95	+0.63	+0.56	+1.19
	2.40	4.89				
	2.87	6.06				

* not measurable owing to very strong acid

a) H.H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

strong. This may be attributed to the steric hindrance. When the substituent group is a chloride or amino group, the pK_{a1} values of these derivatives can be calculated by the iterative approximation method; the pK_{a1} values are (0.6) and (1.2) respectively. The introduction of a chlorine atom to *o*-phenylenediamine decreases the value of pK_{a2}; the same effect is observed in carboxyl and amino groups. The relation between the pK_{a2} and the σ_p values shows a good linearity, but the σ_m values do not show such a good linearity. It is implied that the para-position effect, that is, the mesomeric effect, is the main factor rather than the inductive effect (the meta-position effect). The second dissociation of 3,4-diaminobenzoic acid is due to one of the diammonium protons, while the third dissociation is due to the carboxyl proton, because the pK_a (4.75) is comparable with those of 3-aminobenzoic acid (4.79) and 4-aminobenzoic acid (4.92). Table 2 shows the pK_a values for amino-substituted benzoic acids.

TABLE 2. VALUE OF pK_a FOR AMINO-SUBSTITUTED BENZOIC ACIDS IN WATER[12]

X	*ortho*	*meta*	*para*
(H)	(4.20)	(4.20)	(4.20)
NH_2	4.98	4.79	4.92
NHMe	5.33	5.10	5.04
NMe_2	8.42	5.10	5.03
NH_3^+	2.04	—	—

The pK_a values of *o*-phenylenediamine derivatives with CH_3, H, Cl, or CH_3O as a substituent group at the 4 position, are 4—5. The second dissociation of 1,2,4-triaminobenzene trihydrochloride is depressed to an order of magnitude of 3 by the electron-withdrawing effect of the NH_3^+ group.

Stability Constants. The formation curve was obtained by titration. The values of $\bar{n}$ near the center of the formation curve ($0.9<\bar{n}<1.1$) are omitted, because they are very sensitive to slight experimental errors. Selected values of $\bar{n}$ and [L] were used to calculate the overall chelate stability constants, β_1 and β_2, by the use of the method of least squares on a linear form of the Irving and Rossotti equation. The theoretical formation curve is generated by the stability constants reported in Table 3. As can be seen from Fig. 2, the theoretical formation curve was in good agreement with the experimental one.

When 3,4-diaminobenzoic acid system is treated, the relationship between the equilibrium constants and $\log D_i$ $(i=1,2,\cdots,5)$ is as follows:

$$\log K_{M1} = \log D_1,\ pk_1 = \log D_1 - \log D_2,\ \log K_{ML} = pK_{a3} + \log D_2,\ pk_2 = \log D_3 - \log D_4,\ \log K_{M2} = \log D_3 - \log D_1,\ pk_2' = \log D_4 - \log D_5,\ \log K_{ML_2} = 2pK_{a3} + \log D_5.$$

The pK_{a3} value of the 3,4-diaminobenzoic acid was 4.75; however, the acid-dissociation constant (pK_{a1}) of the Cu(II) chelate was 3.84. The depression of the pK_a value is 0.91 (=4.75−3.84). The pK_a values of benzoic acid and *p*-nitro-benzoic acid are 4.18 and 3.43 respectively.[11] Therefore, the *p*-nitro group has an electron-withdrawing effect of 0.75 pK_a units. The Cu(II) ion has a stronger electron-withdrawing effect than does the *p*-nitro group. The introduction of substituent groups in the 4 position of *o*-phenylenediamine leads to marked changes in the log β_2 value, changes which clearly reveal two effects (inductive and meso-

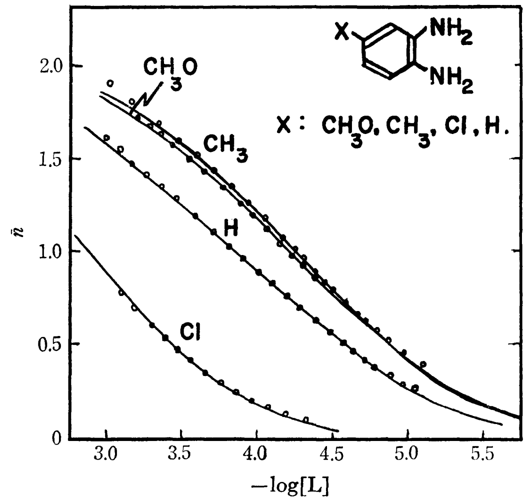
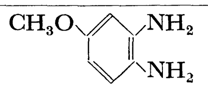
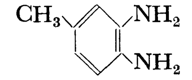
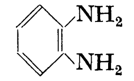
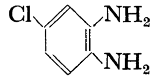


Fig. 2. Experimental and theoretical formation curve, at 25°C and μ=0.10.
—, Theoretical; ○, Experimental

TABLE 3. STABILITY CONSTANTS OF Cu (II) COMPLEXES WITH *o*-PHENYLENEDIAMINE DERIVATIVES

Ligand	log K_1	log K_2	log K_1K_2
	4.78	3.64	8.42
	4.74	3.76	8.50
	4.55	3.17	7.72
	3.32	2.44	5.76

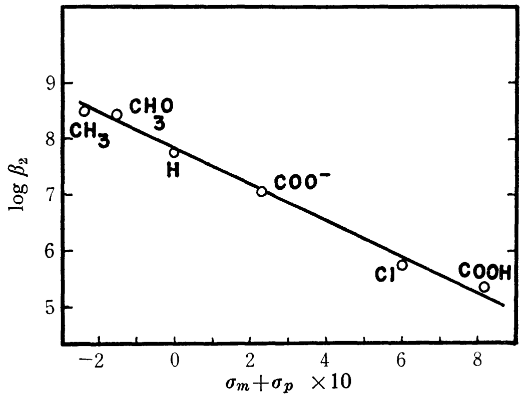


Fig. 3. Relationship between log β_2 and the sum of Hammett's sigma values.

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[11] A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen, London (Japanese Edition, Maruzen) (1962), P. 121.

[12] S. Patai, "The Chemistry of the Amino Group," John Wiley and Sons, London (1968), p. 224.

meric). The plot of log β_2 against the sum of σ_m and σ_p was found to be linear. As can be seen from Fig. 3, the sums of the Hammett's σ_m and σ_p values of the COOH group and the COO$^-$ group are 0.82 and 0.23 respectively. The difference in value between the COOH and COO$^-$ groups is 0.59; that is, the electron-withdrawing effect is decreased after the dissociation, and as a result log β_2 is increased 0.71 units. When the ligand is 1,2,4-triaminobenzene, some converged values were obtained from the metal-ion-excess condition, but different behavior was observed in the ligand-excess condition; therefore, calculation became very difficult. In the reaction between *o*-phenylenediamine and other divalent ions (Mn, Co, Ni, Zn, *etc.*), the pH effect was very small; therefore, their stability constants may be lower.

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