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Copper(II) Complexes of Ethylenediaminemonoacetic Acid (EDMA). A Polarographic Study of the Solution Equilibria between the Copper(II) Ion and EDMA and the Preparation of Copper(II)-EDMA Complexes

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In the present paper, the solution equilibria between the copper(II) ion and ethylenediaminemonoacetic acid (EDMA) were determined polarographically and, then copper(II)-EDMA complexes were prepared and characterized using ion-exchange chromatography and the visible and infrared absorption spectra. Since copper(II) ions in an EDMA solution behave reversibly in a polarographic electrolysis, the composition and the stability constants of copper(II)-EDMA complexes were determined from the dependence of the half-wave potential on the concentration of uncomplexed EDMA by employing a modification of the Deford-Hume method. The copper(II) ion was found to form complexes of 1-to-1 and 1-to-2 compositions with EDMA. Their successive formation constants, K_1 and K_2, were $2.5_2\times10^{13}$ and 1.10×10^{8} respectively. The copper(II)-EDMA complex with a 1-to-1 composition was easily isolated from an aqueous solution of pH 3.0—4.0. On the other hand, the complex with a 1-to-2 composition could be isolated in a low yield by adding ethanol from a solution containing an excess amount of EDMA in the pH range from 10.0 to 11.0. From the infrared spectra and the ion-exchange chromatographic behavior, the ethylenediaminemonoacetate ion in the complexes was concluded to function as a tridentate ligand.

The metal complexes of ethylenediamine and aminopolycarboxylic acids which derived from ethylenediamine have been studied in various aspects, but the investigations of the complexes with ethylenediaminemonoacetic acid (EDMA) as the ligand have been quite limited. In this connection, in order to understand the detailed properties of EDMA as the ligand in the complex formation reaction, it seemed that it would be worthwhile to study thermodynamically the complex formation reaction involving EDMA and to prepare and characterize the metal complexes of EDMA. In this paper, the polarographic determination of the solution equilibria between the copper(II) ion and EDMA and the preparation of copper(II) complexes of EDMA from an aqueous solution will be described. The participation of the acetate group in the complex formation was demonstrated by studying the infrared absorption spectra and by ion-exchange chromatography.

Experimental

Reagents. The ways of preparing and standardizing a standard copper(II) perchlorate solution were given previously.[1] The preparation and purification of EDMA dihydrochloride were also described in a previous paper.[2] Its purity was checked by means of C.H.N. analysis. All the other chemicals used in the polarographic measurements were of an analytical reagent grade.

Apparatus and Experimental Procedures. All the d. c. current-voltage curves were measured by using a manual polarograph similar to that of Kolthoff and Lingane.[3] The rate of the flow of mercury, m, and the drop time, t_d, of the dropping mercury electrode (DME) were 0.839 mg/sec and 3.92 sec respectively, as measured in an air-free 0.10M acetate buffer solution of pH 5.00 with an open-circuit and 70.0 cm of a mercury column at 25°C. A saturated calomel electrode used as the reference electrode has also been described previously.[4] The pH value of the solution was measured with a glass electrode pH meter (Hitachi-Horiba Model M-5). In the pH titration, a semimicroburet with a capacity of 10 ml was used. All the experimental procedures in the polarography were given previously.[4,5] Under the present experimental conditions, the maximum

1) M. Kodama and H. Ebine, This Bulletin, **40**, 1857 (1967).

2) Y. Fujii, E. Kyuno and R. Tsuchiya, *ibid.*, to be published.

3) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 1, Interscience, New York (1952), p. 297.

4) M. Kodama and A. Kimura, This Bulletin, **40**, 1639 (1967).

5) M. Kodama, S. Naito and M. Ebine, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 576 (1963).

of the first kind appeared in the reduction wave of the copper(II) ion in an EDMA solution. Therefore, 6×10^{-6}M LEO (polyoxyethylene lauryl ether) was added to the sample solution in order to surpress it.

All the visible absorption spectra were recorded on a Hitachi EPS-3 pen-recording spectrophotometer using water as a solvent. The infrared absorption spectra were taken on Nujol mulls between sodium chloride plates or potassium bromide disks, using a Hitachi EPI-S2 spectrometer. The magnetic susceptibility was determined by the Gouy method using powdered samples at 24°C.

Methods of Analysis. The carbon, hydrogen, and nitrogen analyses of the solid complexes were performed by the conventional combustion method using a Yanagimoto C.H.N. Corder MT-1. The copper was determined polarographically by measuring the wave-height of the copper(II) ion in an acetate buffer solution of pH 5.0 containing 20.0 mM EDMA.

Results and Discussion

Polarographic Determination of Solution Equilibria between Copper(II) Ions and EDMA. In the theoretical analysis of the polarographic data, accurate pK values of EDMA are necessary. Therefore, the pK values of EDMA were first determined by the potentiometric acid-base titration. Titration was carried out on oxygen-free sample solutions in a beaker-type cell with a water-jacket thermostatted at 25°C. The titration curve of an EDMA with a carbonate-free sodium hydroxide exhibited sharp inflections corresponding to the successive stages of neutralization (Fig. 1). The pK_2 value corresponding to the following dissociation reaction was estimated to be 6.65 from the pH value at the half-titration point.

$$H_2X^+ \overset{pK_2}{\rightleftharpoons} HX + H^+$$

The pK_1 and pK_3 values were then calculated by using the pH values at the first and second inflection points with the aid of the well-known relation (1):[6]

$$pH_i = \frac{(pK_2+pK_j)}{2} \qquad (1)$$

where pH_i denotes the pH at the first or second inflection point, and pK_j, the pK_1 or pK_3 value corresponding to the following proton dissociation equilibria. The estimated pK_1 and pK_3 were 2.15 and 10.15 respectively.

$$H_3X^{2+} \overset{pK_1}{\rightleftharpoons} H_2X^+ + H^+$$

$$HX \overset{pK_3}{\rightleftharpoons} X^- + H^+$$

The copper(II) ion in an EDMA solution invariably gave a single well-defined polarographic wave (Fig. 2). Its wave-height was exactly proportional to the square-root of the effective mercury pressure on the DME and to the bulk concentration of the

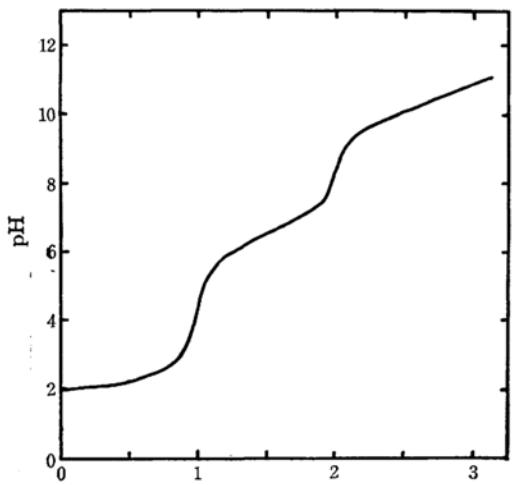

Fig. 1. The pH titration of EDMA with sodium hydroxide solution.
Initial concentration of EDMA dihydrochloride =5.0 mM
Volume of EDMA dihydrochloride solution =100 ml
Concentration of sodium hydroxide solution =0.914M
25°C, μ=0.20

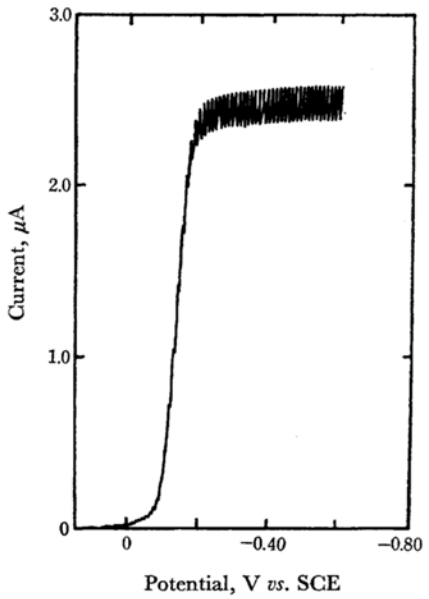

Fig. 2. D.c. polarogram of copper(II) ion in the EDMA solution.
Concentration of copper(II) ion=0.686 mM
Concentration of uncomplexed EDMA=20.0 mM
Concentration of acetate ion=0.10M
Concentration of LEO=6×10^{-6}M
μ=0.20, pH=5.03

6) J. J. Lingane, "Electroanalytical Chemistry," Interscience, New York (1953).

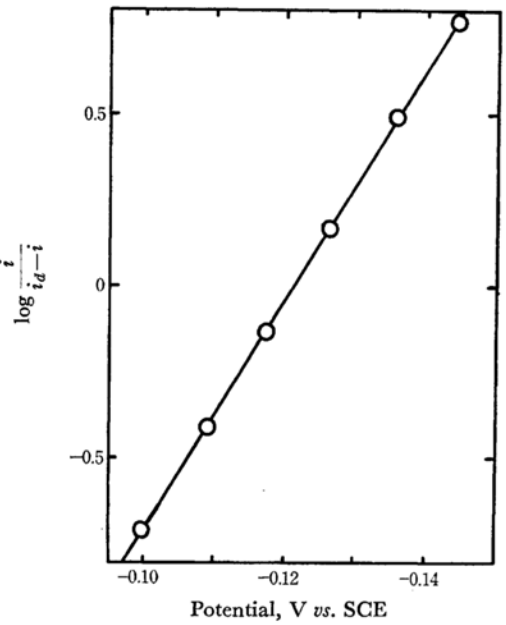

Fig. 3. Log-plot examination.
Concentration of copper(II) ion=0.686 mM
Concentration of uncomplexed EDMA=20.0 mM
Concentration of acetate ion=0.10M
Concentration of LEO=6×10^{-6}M
μ=0.20, pH=5.03

copper(II) ion. At pH's lower than 7.0, the log-plot analysis of the polarogram has a linear relation with a reciprocal slope falling in the range from 33 to 35 mV. A typical example is shown in Fig. 3. Therefore, it can be concluded that the copper(II) ion in the EDMA solution undergoes a two-electron reversible reduction at the mercury electrode. Consequently, the solution equilibria between the copper(II) ion an EDMA can be successfully determined by the conventional polarographic method. Since and EDMA anion has two nitrogen groups and one acetate group, it may act as a tridentate ligand. Therefore, the copper(II) ion may be expected to form the complexes with 1-to-1 and 1-to-2 compositions. If both 1-to-1 and 1-to-2 complexes are formed, the electrode reaction of the copper(II) ion at the mercury electrode can be assumed to be:

$$\begin{array}{l} CuX^{+} + nH^{+} + Hg + 2e^{-} \rightleftharpoons Cu(Hg) + H_nX^{n-1} \\ \quad \downarrow\uparrow \\ \quad CuX_2 \end{array}$$

where CuX^{+} and CuX_2 are copper(II)-EDMA complexes of 1-to-1 and 1-to-2 compositions and where H_nX^{n-1} means the protonated EDMA ion. Hence, the shift of the half-wave potential of the copper(II) ion due to the complex formation can be derived thermodynamically as:

$$\Delta E_{1/2} = (E_{1/2})_{Cu} - (E_{1/2})_{CuX}$$

$$= 0.0296\left[\log\left(\frac{K_1\cdot[X]_f}{(\alpha_H)_X} + \frac{K_1\cdot K_2\cdot[X]^2_f}{(\alpha_H)^2_X}\right) + \log\frac{k_{CuX}}{k_{Cu^{2+}}}\right] \quad (3)$$

where $(E_{1/2})_{Cu}$, $(E_{1/2})_{CuX}$, k_{CuX}, and $k_{Cu^{2+}}$ have their usual meanings[7] and where $(\alpha_H)_X$ and $[X]_f$ denote the (α_H) value of EDMA and the concentration of uncomplexed EDMA respectively. K_1 and K_2 are the successive formation constants of copper(II)-EDMA complexes.

Equation (3) clearly indicates that when the solution pH is kept constant, the plot of (antilog $[\Delta E_{1/2}/0.0296+\log k_{Cu^{2+}}/k_{CuX}])/[X]_f$ against $[X]_f$ will give the linear relation, the slope and the intercept of which correspond to $K_1\cdot K_2/(\alpha_H)^2_X$ and $K_1/(\alpha_H)_X$ respectively. On the other hand, if only the complex with a 1-to-1 composition is formed, the plot of antilog $[\Delta E_{1/2}/0.0296+\log k_{Cu^{2+}}/k_{CuX}]$ against $[X]_f$ should give the linear relation. These relations were examined at pH 5.0. Experiments were carried out on acetate buffer solutions containing an uncomplexed EDMA, because at this pH the system containing only uncomplexed EDMA does not have enough buffer capacity to keep the solution pH constant during the electrolysis. The linear relation shown in Fig. 4 clearly indicates that the copper(II) ion forms complexes of 1-to-1 and 1-to-2 compositions under the present experimental conditions. From the intercept and the slope of the linear relation, the K_1 and K_2 values were estimated to be $2.5_2\times10^{13}$ and 1.10×10^{8} respectively.

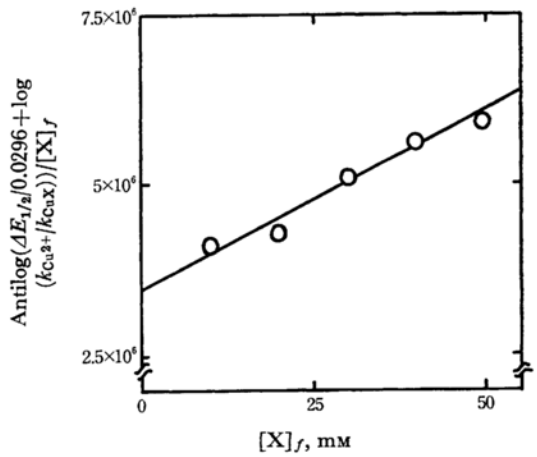

Fig. 4. Determination of successive formation constants of copper(II)-EDMA complexes.
Concentration of copper(II) ion=0.686mM
Concentration of acetate ion=0.10M
Concentration of LEO=6×10^{-6}M
μ=0.20, pH=5.00, 25°C

7) M. Kodama and Y. Tominaga, This Bulletin, **42**, 394 (1969).

Table 1. The effect of acetate or chloride ion on the half-wave potential

μ=0.20, 25°C
Concentration of copper(II) ion=0.686 mM
Concentration of uncomplexed EDMA=20.0 mM

A: Chloride ion effect*

Concentration of chloride ion, M	Half-wave potential V *vs.* SCE
0.040	−0.322
0.187	−0.321

B: Acetate ion effect**

Concentration of Acetate ion, M	Half-wave potential V *vs.* SCE
0.05	−0.126
0.14	−0.124

* pH=7.00, 25°C
No buffer reagent was used because uncomplexed EDMA can serve as a buffer reagent at this pH.
** pH=5.00, 18°C

Table 2. The effect of pH on the half-wave potential

μ=0.20, 25°C
Concentration of copper(II) ion=0.686 mM
Concentration of uncomplexed EDMA=20.0 mM
Concentration of acetate ion=0.10 M

A: Acid medium

pH	Half-wave potential V *vs.* SCE	$\Delta E_{1/2}$, mV obsd	$\Delta E_{1/2}$, mV calcd
5.03	−0.122	0	0
5.59	−0.171	−49	−53.4
6.13	−0.229	−107	−105.9

B: Neutral or weak alkaline medium*

pH	Half-wave potential V *vs.* SCE	$\Delta E_{1/2}$, mV obsd	$\Delta E_{1/2}$, mV calcd
6.90	−0.309	+44	+40.6
7.11	−0.324	+29	+24.7
7.48	−0.353	0	0
7.83	−0.384	−31	−24.0
8.01	−0.397	−44	−35.1

* No buffer reagent was used because uncomplexed EDMA can serve as a buffer reagent in this pH range.

The possible formation of a mixed ligand complex involving acetate or chloride ions could be ruled out by the fact that the half-wave potential was independent of the concentration of acetate or chloride ions, provided that the solution pH and EDMA concentration were kept constant (Table 1). If the above conclusion is correct, the dependence of the half-wave potential on the solution pH must be explained satisfactorily by using the K_1 and K_2 values thus determined. The pH dependence of the half-wave potential was calculated with the aid of Eq. (3) and compared with the observed data. The results are shown in Table 2. In acid and neutral media, the calculated values agreed well with the observed values. In a weak alkaline medium, however, the observed values are slightly larger than the calculated ones. This can be ascribed to the fact that the reversibility of the electrode reaction in a weak alkaline medium is not so complete as in acid and neutral media. This explanation could be confirmed by the value of the reciprocal slope (45 mV).

From all the above results and discussion, it can be concluded that the pK values of EDMA and K_1 and K_2 values of copper(II)-EDMA complexes thus determined are reasonable.

Characterization of Copper(II)-EDMA Complexes. Since the formation of copper(II)-EDMA complexes of 1-to-1 and 1-to-2 compositions was confirmed polarographically, we tried to prepare and characterize these complexes. Although, because of kinetic, solubility and other limitations, the predominant species in the solution can not always be separated selectively from the equilibrium mixture, for the successful preparation of metal complexes, it seems that its formation reaction in solution had better to be complete in a thermodynamic sense. Therefore, in order to find the optimum conditions for the preparation, we first calculated the fraction of the copper(II) ion present in each species of the copper(II)-EDMA complex using the pK values of EDMA and the formation constants of copper(II)-EDMA complexes with the aid of the following relations:

$$[\mathrm{Cu}]_t = [\mathrm{Cu}^{2+}] + [\mathrm{CuX}^+] + [\mathrm{CuX}_2]$$

$$[\mathrm{X}]_t = [\mathrm{X}]_f + [\mathrm{CuX}^+] + 2\cdot[\mathrm{CuX}_2]$$

$$\frac{K_1}{(\alpha_H)_X} = \frac{[\mathrm{CuX}^+]}{[\mathrm{Cu}^{2+}]\cdot[\mathrm{X}]_f}, \quad \frac{K_2}{(\alpha_H)_X} = \frac{[\mathrm{CuX}_2]}{[\mathrm{CuX}^+]\cdot[\mathrm{X}]_f}$$

Table 3. The fraction of copper(II) ion presents as each species of copper(II)-EDMA complex

Total concentration of copper(II)=0.80 M

pH	Total concentration of EDMA, M	Fraction Cu^{2+}	CuX^+	CuX_2
3.0	0.80	5.8×10^{-2}	9.41×10^{-1}	6.6×10^{-4}
4.0	0.80	2.0×10^{-3}	9.96×10^{-1}	2.0×10^{-3}
10.0	3.20	3.6×10^{-22}	9.1×10^{-9}	1.00
11.0	3.20	8.2×10^{-23}	4.3×10^{-9}	1.00

where $[Cu]_t$ and $[X]_t$ mean the total concentrations of copper(II) and EDMA respectively, and $[CuX^+]$ and $[CuX_2]$, the concentrations of copper(II)-EDMA complexes of 1-to-1 and 1-to-2 compositions. The results summarized in Table 3 clearly indicate that the copper(II) ion in the solution of pH 3.0—4.0, which is 0.80M with respect to copper(II) and 0.80M with respect to EDMA, exists predominantly in the form of CuX^+ and that the copper(II) ion in the solution of pH 10.0—11.0 containing 0.80M copper(II) and 3.20M EDMA exists only in the form of CuX_2. On the basis of the above thermodynamic information, we tried to prepare the copper(II)-EDMA complexes. The complex with a 1-to-1 composition could be prepared and isolated from the solution of pH 3.0—4.0, and that with a 1-to-2 composition, from the solution of pH 10.0—11.0 containing an excess of EDMA, as will be described below.

Preparation of Ethylenediaminemonoacetatoaquocopper(II) Chloride Monohydrate. To 50 m*l* of an aqueous solution containing 3.4 g (0.02 mol) copper(II) chloride dihydrate, about 4.2 g (0.02 mol) of EDMA·2HCl·H_2O were added. After adjusting the solution pH to 3.0—4.0 by adding a 6N sodium hydroxide solution, the mixture solution was heated on a water bath until its volume was reduced to 25 m*l*. When the resulting solution was cooled to 0°C, light blue crystals were deposited and filtered off. This crude product was then recrystallized from a 50% ethanol solution. The yield was 1.5 g (approximately 30%). Found: Cu, 24.6; C, 18.78; H, 4.87; N, 11.14%. Calcd for [Cu(EDMA)(H_2O)]Cl·H_2O: Cu, 25.2; C, 19.04; H, 5.21; N, 11.11%.

Preparation of Bis(ethylenediaminemonoacetato)copper(II) Tetrahydrate. To 50 m*l* of an aqueous solution containing 3.4 g (0.02 mol) copper(II) chloride dihydrate, about 16.0 g (0.08 mol) EDMA·2HCl·H_2O were added. After the resulting mixture had been heated on a water bath for ten minutes, the solution pH was adjusted to 10.0—11.0 by adding a 6N sodium hydroxide solution. The mixture solution was then evaporated naturally to about 10 m*l*, whereby the sodium chloride thus deposited was filtered off. At this point, ethanol (80—100 m*l*) was added to the solution. The resulting mixture was then cooled to 0°C and allowed to stand in a refrigerator for 2—3 weeks. Dark blue crystals were obtained. The yield was about 10%. Found: Cu, 16.6; C, 26.01; H, 6.65; N, 15.41%. Calcd for [Cu(EDMA)$_2$]·$4H_2O$: Cu, 17.2; C, 25.97; H, 7.10; N, 15.15%.

Table 4. The visible and IR spectra of the copper(II)-EDMA complexes

Compound	λ_{max} (c/s) $\times 10^{-13}$	log ε	Carboxylate asym. str., cm^{-1}
$[Cu(H_2O)_6^{2+}]$	36.5	1.09	—
[Cu(EDMA)(H_2O)]Cl·H_2O	44.4	1.62	1600
[Cu(EDMA)$_2$]·$4H_2O$	49.2	1.86	1626
EDMA·2HCl·H_2O	—	—	1730

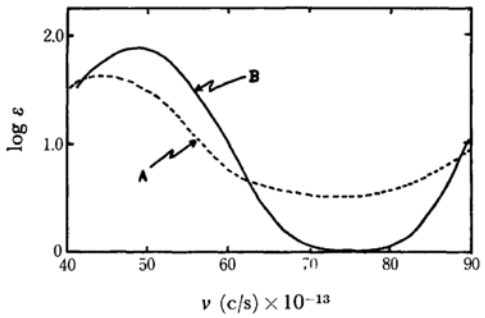

Fig. 5. Visible absorption spectra of copper(II)-EDMA complexes.
Concentration of uncomplexed EDMA=10.0 mM
A: pH=4.0, Acetate buffer solution (0.10M), the complex with 1-to-1 composition
B: pH=7.0, The complex with 1-to-2 composition

As is shown by the visible absorption spectra in Fig. 5, the copper(II)-EDMA complexes of 1-to-1 and 1-to-2 compositions gave absorption maxima at 44.4×10^{13} and 49.2×10^{13} sec^{-1} respectively. The maxima can be regarded as the peaks due to the d–d transition. The large shift of the absorption curve to the higher energies may be a strong indication that the nitrogen groups of EDMA are coordinated to the copper(II) ion[8,9] (Table 4). Since the visible absorption study can not give any confirmative information about the participation of the acetate group in the coordination bond formation, the infrared (IR) study was carried out. The IR absorption spectrum of dark blue crystal was measured in a potassium bromide disk, but that of light blue crystal, in a Nujol-mull state. Because, in the case of light blue crystal, the color of the potassium bromide disk changed from light blue to yellow. This can be ascribed to the formation of a mixed ligand complex involving the bromide ion. As the spectral data in Table 4 show, the light blue and dark blue crystals show the strong bands of the carboxylate group at 1600 and 1626 cm^{-1} respectively. Generally, the uncoordinated $-COO^-$ group of aminopolycarboxylic acid has been observed to exhibit its characteristic band in the range from 1610 to 1580 cm^{-1}, and the –COOH group, from 1750 to 1690 cm^{-1}.[10] Therefore, the above two bands of copper(II)-EDMA

8) T. Dreisch and W. Trommer, *Z. Phys. Chem.*, **37**, 37 (1937).
9) M. Kubota, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **62**, 509 (1941).
10) T. Sakaguchi and K. Ueno, "Metal Chelates," Vol. II, Nankodo, Tokyo (1963), p. 43.

complexes can probably be ascribed to the coordinated carboxylate group.

The ion-exchange chromatographic study also supports the above interpretation. In the aqueous solution of the light blue crystal (pH=4.0; concentration of uncomplexed EDMA=10.0 mM), the cation exchange regin (Dowex 50W-X8, 100—200 mesh) in the Na^+ form could capture the copper(II) ion effectively, but the anion exchange regin (Dowex 1-X8, 100—200 mesh) in the Cl^- form could not. On the other hand, in the case of the solution containing the dark blue crystal (pH=7.0; concentration of uncomplexed EDMA=10.0 mM), neither ion-exchange resin could capture the copper(II) ion. These facts clearly indicate that the copper(II) ion in the former solution exists as a positively-charged species, but in the latter solution, as a zero-charged species, suggesting the participation of the carboxylate group in the complex formation.

The possibility of the formation of the dimer structure in the crystal state could be ruled out by the magnetic susceptibility measurements (1.75 B.M. for the light blue crystal and 1.92 B.M. for the dark blue crystal).[11]

From the above results and discussion, we have concluded that the light blue crystal isolated from an acid solution is $[Cu(EDMA)(H_2O)]Cl \cdot H_2O$, corresponding to the square planar structure, and that the dark blue crystal obtained from the alkaline medium is $[Cu(EDMA)_2] \cdot 4H_2O$, corresponding to the octahydral structure.

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11) K. Gora, E. Kyuno and R. Tsuchiya, This Bulletin, **41**, 2624 (1968).