Mixed-ligand Complexes of Copper(II). II. A Study of Dismutation Constants

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The dismutation constants for mixed-ligand complexes of copper(II) involving, as bidentate ligands, ethylenediamine, L-alanine, β-alanine, and *N,N*-dimethylglycine were determined at two or three temperatures by both the spectrophotometric and ESR methods, and the thermodynamic constants were then derived from those data. It was found for these systems that the entropy change plays a main role in governing the equilibrium between a mixed-ligand complex and its parent complexes, and that the differences in the dismutation constants among the mixed-ligand complexes are due to the small but different values of the enthalpy term.

When two kinds of stable copper(II) complexes with bidentate ligand (A and B) are dissolved in a solvent, the following kind of equilibrium is generally established in the solution:

$$\mathrm{CuA_2} + \mathrm{CuB_2} \rightleftharpoons 2\mathrm{CuAB} \tag{1}$$

$$K = \frac{[\mathrm{CuAB}]^2}{[\mathrm{CuA_2}][\mathrm{CuB_2}]} \tag{2}$$

The reciprocal of K is designated by Watters *et al.* as the dismutation constant.[1] The studies of the equilibrium and of the coordinate bond for the mixed-ligand complexes seem to be important in coordination chemistry and in biochemistry, since these studies are concerned with extending such a fundamental concept as soft and hard acids and bases,[2] and since the mixed-ligand complexes are regarded as models for metalloenzyme-substrate complexes.[3,4] Furthermore, the complexes are important in analytical chemistry and in synthetic reactions catalyzed by metal ions.[5,6] Many studies of mixed-ligand complexes have been mainly concerned with their stability.[1,7-10]

In a previous paper,[11] we reported on an ESR study of the coordinate bond for mixed-ligand complexes with comparatively large K values, using, as bidentate ligands, ethylenediamine, its analogues, and amino acids. We pointed out that, for the two systems with ethylenediamine and β-alanine as A and B in Eq. (1) and with ethylenediamine and *N,N*-dimethylglycine, two or three complex species can clearly be identified from the ESR spectra in the solution, since the K values of these systems are comparatively small. The purpose of this paper is to investigate in full detail, by the use of both the spectrophotometric and ESR techniques, what factors govern the above-mentioned equilibrium, using as the parent complexes the 1:2 complexes of copper(II) with ethylenediamine, L-alanine, β-alanine, and *N,N*-dimethylglycine.

Experimental

The copper(II) complexes employed in this work, which had been prepared and purified in a previous work,[11] were $[\mathrm{Cu(en)_2}](\mathrm{ClO_4})_2$, $[\mathrm{Cu(L\text{-}Ala)_2}]$, $[\mathrm{Cu(\beta\text{-}Ala)_2}]\cdot 6\mathrm{H_2O}$, and $[\mathrm{Cu(dmg)_2}]\cdot 3\mathrm{H_2O}$, where en, L-Ala, β-Ala, and dmg are ethylenediamine and the anions of L-alanine, β-alanine, and *N,N*-dimethylglycine respectively. The sample solutions for the ESR and optical absorption measurements were 1.00×10^{-2} mol/l solutions of these four complexes and mixtures of any two of the solutions at various volume ratios, with an equivolume mixture of water and methanol being used as the solvent.

The ESR spectra of these sample solutions were measured at the temperature of liquid nitrogen with a Hitachi X-band ESR spectrometer, Model MES-4001, equipped with a 100 kHz field modulation unit. The field was calibrated with an NMR probe, and then with a benzene solution of vanadyl acetylacetonate. The optical absorption spectra were measured at temperatures of 20 and 50°C with a Hitachi spectrophotometer, Model EPS-3T, in the range from 340 to 700 mμ, using 10-mm quartz cells.

Results

The 1.00×10^{-2} mol/l solutions (solvent: an equivolume mixture of water and methanol) of $[\mathrm{Cu(en)_2}](\mathrm{ClO_4})_2$, $[\mathrm{Cu(L\text{-}Ala)_2}]$, $[\mathrm{Cu(\beta\text{-}Ala)_2}]\cdot 6\mathrm{H_2O}$, and $[\mathrm{Cu(dmg)_2}]\cdot 3\mathrm{H_2O}$ will hereafter be designated as Systems

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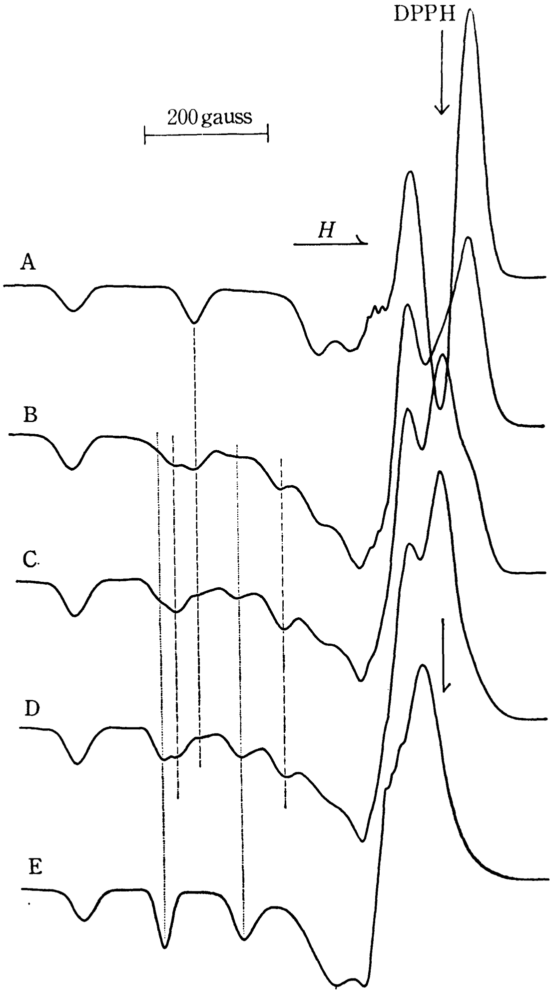

Fig. 1. The X-band ESR spectra (measured at 77°K, 1.00×10^{-2} mol/*l* per copper atom, Solvent: an equivolume mixture of water and methanol) of the mixed solutions of $[Cu(en)_2]^{2+}$ and $[Cu(\beta\text{-}Ala)_2]$ at the following molar ratios: (A) 1 : 0, (B) 2 : 1, (C) 1 : 1, (D) 1 : 2, and (E) 0 : 1. Each of the vertical lines shown at the low field part locates an absorption line due to one of the three molecular species.

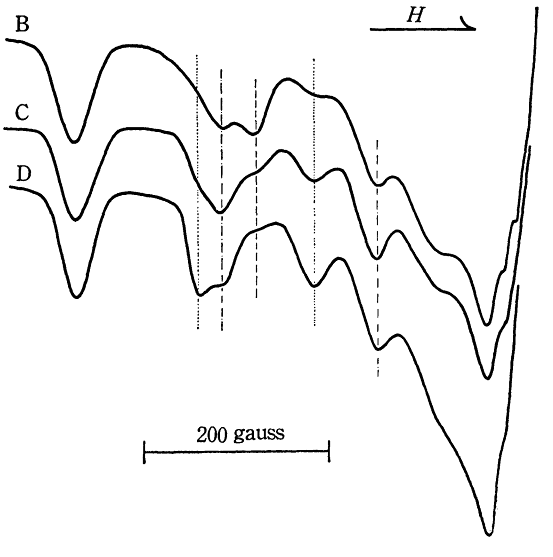

Fig. 2. Some of the enlarged ESR spectra of Fig. 1 at the low field part (the spectral names and the vertical lines are those referred to in Fig. 1).

I, II, III, and IV. The mixture of I and II, for example, is described as System I–II, and the volume ratio in the mixture is affixed to this expression in parentheses.

Determination of K by ESR. The ESR spectra of Systems I–II (1:1) and II–III (1:1), measured at the temperature of liquid nitrogen, which had already been presented in a previous paper,[11] indicated that the mixed-ligand complexes are almost quantitatively formed in the solution of these systems, and it was expected that the *K* values for these systems would be comparatively large. Attention must, however, be paid to the fact that the *K* values under discussion are determined at a certain temperature immediately before the sample solutions freeze in liquid nitrogen (sample glass tubes about 4 mm in diameter are directly immersed in liquid nitrogen in this study). Since the exact freezing temperature of these solutions on such rapid cooling is unknown, the temperature was assumed to be about −100°C in this work.[12] On the other hand, it was reported in a previous paper that the ESR spectra of Systems I–III (1:1) and I–IV (1:1) are not due to a single complex species, suggesting that the *K* values of these systems are remarkably small as compared with those of other systems.[11] In this study we made an attempt to determine the *K* values for these two systems from the ESR spectra, as will be described below.

The ESR spectra of System I–III at various volume ratios are shown in Fig. 1, while the enlarged spectra in the low-field part of Fig. 1 are shown in Fig. 2. These two figures clearly indicate that the ESR spectra are made up of the superposition of three different spectra; three complex species coexist in System I–III. It can easily be understood that the three complex species correspond to the two parent complexes and one mixed-ligand complex. If the molar ratio of these three complexes can be properly estimated from the ESR spectra, the *K* value can be calculated using Eq. (2). The hyperfine absorption lines of $I_z = -1/2$ for the three complexes appear near the base line in the low-field part, this fact being a factor in attaining greater accuracy in the following analysis, and the lines are superposed to a moderate extent upon each other, whereas the absorption lines of $I_z = -3/2$ overlap to too complete a degree to be analyzed. The most reasonable method for analyzing the ESR spectra with the aim of determining the molar ratio, therefore, seems to consist in resolving the spectral part of the overlapping absorption lines of $I_z = -1/2$ into the corresponding three components, and then in properly deriving the molar ratio from the resolved spectra.

It was assumed that the observed ESR line shape can

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[12] The freezing temperature of the equivolume mixture of water and methanol is −47°C ("The Merck Index," eighth edition ed. by P. G. Stecher, Merck & Co., Inc., New Jersey, U.S.A. (1968), p. 671). The freezing temperature of the sample solutions under discussion, however, is considered to be further lowered to a very large extent on such extremely rapid cooling as we adopted, since it has been reported that, when the cooling rate is increased, the freezing temperature of water is lowered owing to the phenomenon of supercooling (I. E. Kuhns and B. J. Mason, *Proc. Roy. Soc.* (London), **A302**, 437 (1968)).

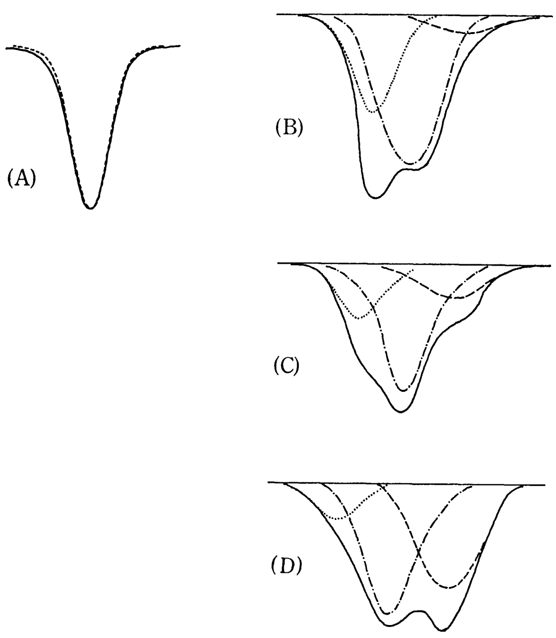

Fig. 3. The overlapping hyperfine absorption lines of $I_z = -1/2$ resolved into three components by the Gaussian analysis for the mixed solutions of $[Cu(en)_2]^{2+}$ and $[Cu(\beta\text{-Ala})_2]$ at the following molar ratios: (A) 0 : 1, (B) 1 : 2, (C) 1 : 1, and (D) 2:1.

be approximated by the following Gaussian curve:

$$S_i(H) = b \exp\left(-a^2(H_i^\circ - H)^2\right)$$
$$a = \sqrt{2}/\Delta H_i^{\mathrm{msl}},$$
$$b = \sqrt{2/\pi}/\Delta H_i^{\mathrm{msl}}, \quad \Delta H_i^{\mathrm{msl}} = \Delta H_i/1.386$$

where ΔH_i is the half-width; $\Delta H_i^{\mathrm{msl}}$, the separation between the points of the maximum and minimum slopes, and H_i°, the magnetic field at the center of an absorption line, i. In order to check whether or not the Gaussian curve can simulate the observed absorption lines of $I_z = -1/2$ with a good approximation, the observed absorption line of System III was compared with a Gaussian curve; the results are shown in Fig. 3 (A). This figure suggests that the observed spectra can be analyzed by the Gaussian curves with a fairly good approximation.

The values of ΔH_i for the absorption lines of $I_z = -1/2$ of $[Cu(en)_2]^{2+}$ and $[Cu(\beta\text{-Ala})_2]$ were determined from their ESR spectra to be 17 and 12.5 gauss respectively. Some of the results obtained by this analysis are shown in Fig. 3, using 15 gauss as the ΔH_i value of the mixed-ligand complex. It is, furthermore, assumed that the molar ratio of the three complexes is approximately proportional to the ratio of the integrated intensities of the corresponding resolved Gaussian curves. This seems to be a reasonable assumption, since the three complexes are not extremely different from each other in their magnetic parameters. The ESR spectra of System I–IV, some of which are shown in Fig. 4, were analyzed in a similar way. The analysis for this system, however, was more difficult than for

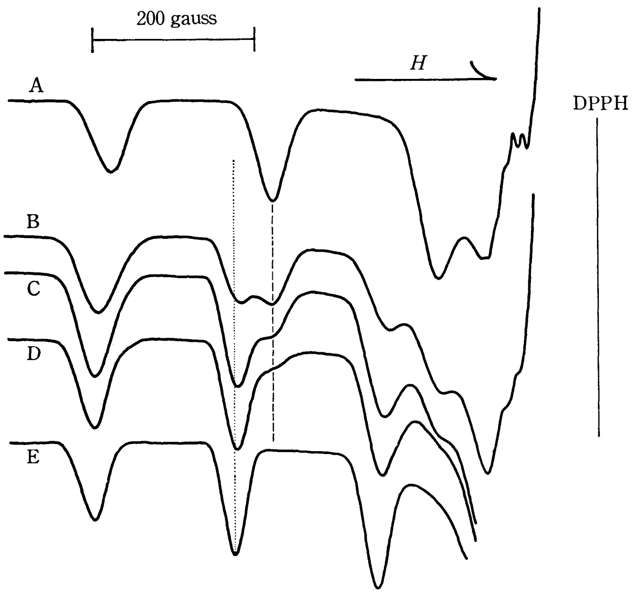

Fig. 4. The X-band ESR spectra (measured at 77°K, 1.00×10^{-2} mol/l per copper atom, Solvent: an equivolume mixture of water and methanol) of the mixed solutions of $[Cu(en)_2]^{2+}$ and $[Cu(dmg)_2]$ at the following ratios: (A) 1 : 0, (B) 2 : 1, (C) 1 : 1, (D) 1 : 2, and (E) 0 : 1. The absorption line of $I_z = -1/2$ of the mixed ligand complex, the location of which is not apparent in the line shape, appears between the two vertical dotted lines on the figure.

TABLE 1. MOLAR RATIO DETERMINED FROM ESR SPECTRA[a] BY GAUSSIAN ANALYSIS FOR THE EQUILIBRIUM $[Cu(en)_2]^{2+} + [Cu(\beta\text{-Ala})_2] \rightleftharpoons 2[Cu(en)(\beta\text{-Ala})]^+$

$c_1 \times 10^2$ [b]	$c_2 \times 10^2$ [b]	$[Cu(en)_2]^{2+}$	$[Cu(\beta\text{-Ala})_2]$	$[Cu(en)(\beta\text{-Ala})]^+$	log K
2/3	1/3	0.43	0.11	0.46	0.65
7/11	4/11	0.36	0.13	0.51	0.74
3/5	2/5	0.33	0.16	0.51	0.71
5/9	4/9	0.25	0.20	0.55	0.78
1/2	1/2	0.18	0.21	0.61	0.99
3/7	4/7	0.16	0.27	0.57	0.88
1/3	2/3	0.14	0.34	0.52	0.75
				Mean value:	0.79±0.04

a) measured at 77°K, Solvent: an equivolume mixture of water and methanol.

b) c_1 and c_2 are the initial concentrations (mol/l) of $[Cu(en)_2]^{2+}$ and $[Cu(\beta\text{-Ala})_2]$ respectively.

TABLE 2. MOLAR RATIO DETERMINED FROM ESR SPECTRA[a] BY GAUSSIAN ANALYSIS FOR THE EQUILIBRIUM $[Cu(en)_2]^{2+} + [Cu(dmg)_2] \rightleftharpoons 2[Cu(en)(dmg)]^+$

$c_1 \times 10^2$ [b]	$c_2 \times 10^2$ [b]	$[Cu(en)_2]^{2+}$	$[Cu(dmg)_2]$	$[Cu(en)(dmg)]^+$	log K
4/5	1/5	0.59	0.19	0.22	$\bar{1}.64$
2/3	1/3	0.48	0.32	0.20	$\bar{1}.42$
3/5	2/5	0.44	0.34	0.22	$\bar{1}.51$
1/2	1/2	0.32	0.44	0.24	$\bar{1}.61$
2/5	3/5	0.24	0.51	0.25	$\bar{1}.71$
1/3	2/3	0.17	0.64	0.19	$\bar{1}.52$
1/5	4/5	0.11	0.74	0.15	$\bar{1}.44$
				Mean value:	$\bar{1}.55 \pm 0.04$

a) measured at 77°K, solvent: an equivolume mixture of water and methanol.

b) c_1 and c_2 are the initial concentrations (mol/l) of $[Cu(en)_2]^{2+}$ and $[Cu(dmg)_2]$ respectively.

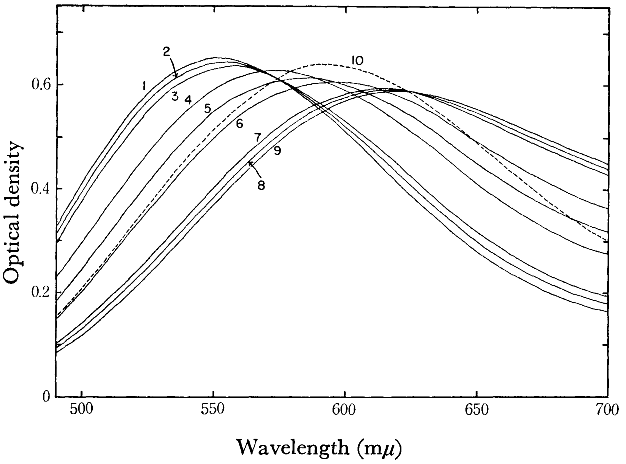

Fig. 5. The visible absorption spectra (measured at 20°C, solvent: an equivolume mixture of water and methanol) of the mixed solutions of $[Cu(en)_2]^{2+}$ and $[Cu(L\text{-}Ala)_2]$.

Curve	$c_1 \times 10^2$	$c_2 \times 10^2$
1	1	0
2	0.95	0.05
3	0.9	0.1
4	2/3	1/3
5	1/2	1/2
6	1/3	2/3
7	0.1	0.9
8	0.05	0.95
9	0	1
10	curve of $[Cu(en)(L\text{-}Ala)]^+$ (calcd)	

c_1: initial concentration (mol/*l*) of $[Cu(en)_2]^{2+}$
c_2: initial concentration (mol/*l*) of $[Cu(L\text{-}Ala)_2]$

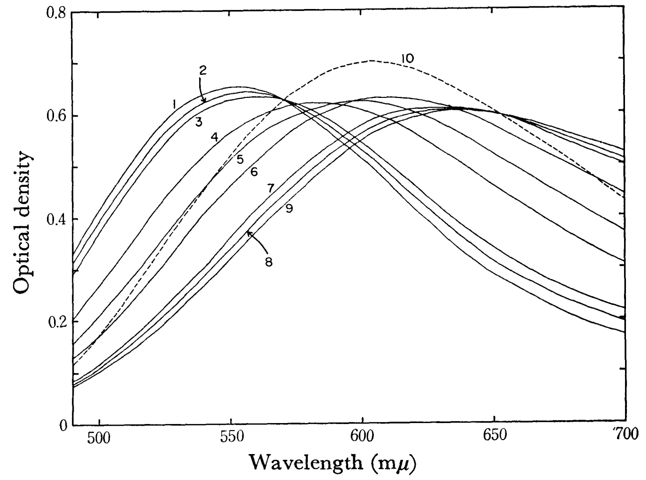

Fig. 6. The visible absorption spectra (measured at 20°C, solvent: an equivolume mixture of water and methanol) of the mixed solutions of $[Cu(en)_2]^{2+}$ and $[Cu(\beta\text{-}Ala)_2]$. The numbering for curves is the same as the one in Fig. 5.

System I–III, since the magnetic parameters of the three complexes for the former system were closer to each other and its *K* value was much smaller. It seems, therefore, that the error accompanying this analysis in System I–IV will inevitably become larger. All the results obtained are listed in Tables 1 and 2, together with the calculated values of log *K*. It seems that much reliance can be placed on this ESR method, since the determined values of log *K* were held constant to a considerable extent for all the mixtures at various volume ratios.

Determination of K by Optical Absorption. The values of *K* were also determined at temperatures of 20 and 50°C by optical absorption measurements according to the Kida method.[7] Some of the observed spectra for Systems I–II and I–III are shown in Figs. 5 and 6 respectively. The spectral measurements for System II–III was carried out only at 20°C in a similar way; an especially careful experiment was required in order to obtain the exact isosbestic points, since the parent complexes are comparatively close to each other in the wavelength and the intensity of the maximum absorption. All the results obtained are listed in Tables 3—6, together with the calculated values of log *K*.

TABLE 3. RESULTS OF THE VISIBLE ABSORPTION MEASUREMENTS ON THE EQUILIBRIUM $[Cu(en)_2]^{2+} + [Cu(L\text{-}Ala)_2] \rightleftharpoons 2[Cu(en)(L\text{-}Ala)]^+$

Temperature (°C)	Wavelength (mμ)	$c_1 \times 10^2$	$c_2 \times 10^2$	D	ε_1	ε_2	ε_3	log *K*
20	574	2/3	1/3	0.614	62.0	48.3	ε_1	1.35
	574	1/2	1/2	0.603	62.0	48.3	ε_1	1.53
	574	1/3	2/3	0.570	62.0	48.3	ε_1	1.46
	615	2/3	1/3	0.529	44.1	58.0	ε_2	1.51
	615	1/2	1/2	0.562	44.1	58.0	ε_2	1.42
	615	1/3	2/3	0.575	44.1	58.0	ε_2	1.39
						Mean value:		1.44±0.02
50	576	2/3	1/3	0.613	63.8	48.3	ε_1	1.41
	576	1/2	1/2	0.614	63.3	48.3	ε_1	1.33
	576	1/3	2/3	0.580	63.8	48.3	ε_1	1.41
	623	2/3	1/3	0.526	43.7	57.8	ε_2	1.44
	623	1/2	1/2	0.558	43.7	57.8	ε_2	1.38
	623	1/3	2/3	0.572	43.7	57.8	ε_2	1.30
						Mean value:		1.38±0.02

c_1, c_2: initial concentrations (mol/*l*) of $[Cu(en)_2]^{2+}$ and $[Cu(L\text{-}Ala)_2]$ respectively.
D: optical density of the solution.
ε_1, ε_2, ε_3: molar extinction coefficients of $[Cu(en)_2]^{2+}$, $[Cu(L\text{-}Ala)_2]$, and $[Cu(en)(L\text{-}Ala)]^+$ respectively.

TABLE 4. RESULTS OF THE VISIBLE ABSORPTION MEASUREMENTS ON THE EQUILIBRIUM $[\mathrm{Cu(en)_2}]^{2+} + [\mathrm{Cu}(\beta\text{-Ala})_2] \rightleftharpoons 2[\mathrm{Cu(en)}(\beta\text{-Ala})]^+$

Temperature (°C)	Wavelength (mμ)	$c_1\times10^2$	$c_2\times10^2$	D	ε_1	ε_2	ε_3	log K
20	570	2/3	1/3	0.614	63.9	39.5	ε_1	0.67
	570	1/2	1/2	0.585	63.9	39.5	ε_1	0.78
	570	1/3	2/3	0.539	63.9	39.5	ε_1	0.93
	654	2/3	1/3	0.434	27.3	56.0	ε_2	0.64
	654	1/2	1/2	0.495	27.3	56.0	ε_2	0.76
	654	1/3	2/3	0.536	27.3	56.0	ε_2	0.87
							Mean value:	0.78±0.04
50	568	2/3	1/3	0.631	65.7	40.5	ε_1	0.67
	568	1/2	1/2	0.602	65.7	40.5	ε_1	0.83
	568	1/3	2/3	0.553	65.7	40.5	ε_1	0.90
	656	2/3	1/3	0.451	28.7	57.5	ε_2	0.73
	656	1/2	1/2	0.511	28.7	57.5	ε_2	0.80
	656	1/3	2/3	0.551	28.7	57.5	ε_2	0.86
							Mean value:	0.80±0.03

c_1, c_2: initial concentrations (mol/l) of $[\mathrm{Cu(en)_2}]^{2+}$ and $[\mathrm{Cu}(\beta\text{-Ala})_2]$ respectively.
D: optical density of the solution.
ε_1, ε_2, ε_3: molar extinction coefficients of $[\mathrm{Cu(en)_2}]^{+2}$, $[\mathrm{Cu}(\beta\text{-Ala})_2]$, and $[\mathrm{Cu(en)}(\beta\text{-Ala})]^+$ respectively.

TABLE 5. RESULTS OF THE VISIBLE ABSORPTION MEASUREMENTS ON THE EQUILIBRIUM $[\mathrm{Cu(en)_2}]^{2+} + [\mathrm{Cu(dmg)_2}] \rightleftharpoons 2[\mathrm{Cu(en)(dmg)}]^+$

Temperature (°C)	Wavelength (mμ)	$c_1\times10^2$	$c_2\times10^2$	D	ε_1	ε_2	ε_3	log K
20	542	2/3	1/3	0.611	65.2	57.2	ε_2	0.09
	542	1/2	1/2	0.597	65.2	57.2	ε_2	0.16
	542	1/3	2/3	0.585	65.2	57.2	ε_2	0.09
	554	2/3	1/3	0.668	65.9	71.0	ε_1	0.14
	554	1/2	1/2	0.676	65.9	71.0	ε_1	0.07
	554	1/3	2/3	0.684	65.9	71.0	ε_1	0.31
							Mean value:	0.14±0.03
50	536	2/3	1/3	0.583	64.0	52.7	ε_2	0.21
	536	1/2	1/2	0.564	64.0	52.7	ε_2	0.03
	536	1/3	2/3	0.544	64.0	52.7	ε_2	0.21
	558	2/3	1/3	0.684	66.8	76.5	ε_1	0.11
	558	1/2	1/2	0.699	66.8	76.5	ε_1	0.15
	558	1/3	2/3	0.714	66.8	76.5	ε_1	0.20
							Mean value:	0.15±0.03

c_1, c_2: initial concentrations (mol/l) of $[\mathrm{Cu(en)_2}]^{2+}$ and $[\mathrm{Cu(dmg)_2}]$ respectively.
D: optical density of the solution.
ε_1, ε_2, ε_3,: molar extinction coefficients of $[\mathrm{Cu(en)_2}]^{2+}$, $[\mathrm{Cu(dmg)_2}]$, and $[\mathrm{Cu(en)(dmg)}]^+$ respectively.

TABLE 6. RESULTS OF THE VISIBLE ABSORPTION MEASUREMENTS AT 20°C ON THE EQUILIBRIUM $[\mathrm{Cu(L\text{-}Ala)_2}] + [\mathrm{Cu}(\beta\text{-Ala})_2] \rightleftharpoons 2[\mathrm{Cu(L\text{-}Ala)}(\beta\text{-Ala})]$

Wavelength (mμ)	$c_1\times10^2$	$c_2\times10^2$	D	ε_1	ε_2	ε_3	log K
600	0.7	0.3	0.561	56.2	53.9	ε_1	1.20
600	0.5	0.5	0.559	56.2	53.9	ε_1	1.32
600	0.3	0.7	0.552	56.2	53.9	ε_1	1.20
						Mean value:	1.24±0.03

c_1, c_2,: initial concentrations (mol/l) of $[\mathrm{Cu(L\text{-}Ala)_2}]$ and $[\mathrm{Cu}(\beta\text{-Ala})_2]$ respectively.
D: optical density of the solution.
ε_1, ε_2, ε_3,: molar extinction coefficients of $[\mathrm{Cu(L\text{-}Ala)_2}]$, $[\mathrm{Cu}(\beta\text{-Ala})_2]$, and $[\mathrm{Cu(L\text{-}Ala)}(\beta\text{-Ala})]$ respectively.

Discussion

All the values of log K are summarized in Table 7; the values of K for Systems I–II, I–III, I–IV, and II–III are about 26, 6, 1, and 17 respectively. The K values of the second and third systems are comparatively smaller than those of the others. This is consistent with the following ESR result: the coexistence of three complex species for Systems I–III and I–IV was clearly established by a study of their ESR spectra. On the other hand, for Systems I–II and II–III the ESR absorption lines due to the parent complexes are very

Table 7. The value of log K

Temperature (°C)	System$^{a)}$			
	I–II	I–III	I–IV	II–III
50	1.38 ± 0.02	0.80 ± 0.03	0.15 ± 0.03	——
20	1.44 ± 0.02	0.78 ± 0.04	0.14 ± 0.03	1.24 ± 0.03
ca. $-100^{b)}$	——	0.79 ± 0.10	-0.45 ± 0.15	——

a) Systems I–II, I–III, I–IV, and II–III were designated as the mixed solutions of $[Cu(en)_2]^{2+}$ and $[Cu(\text{L-Ala})_2]$, of $[Cu(en)_2]^{2+}$ and $[Cu(\beta\text{-Ala})_2]$, of $[Cu(en)_2]^{2+}$ and $[Cu(dmg)_2]$, and of $[Cu(\text{L-Ala})_2]$ and $[Cu(\beta\text{-Ala})_2]$ respectively.

b) See the text.

difficult to detect in the spectra; only the mixed-ligand complexes are almost quantitatively formed for Systems I–II and II–III.[11] It is, furthermore, interestingly shown in the table that the values of log K determined by both the optical absorption and ESR methods are almost equal to each other for System I–III and are comparable in their order for System I–IV. These results suggest that the value of K does not depend largely upon the temperature and that this ESR method is an excellent one for determining the K values.

Kida definded log K_{stab} as follows:[7,8]

$$\log K_{\text{stab}} = \log K - \log K_{\text{stat}}$$

where K_{stat} is the value of K when the three complexes in Eq. (1) are distributed entirely statistically or randomly. Under these conditions, K_{stat} is equal to 4: accordingly, log $K_{\text{stat}}=0.60$. If log K_{stab} is positive for a system, the mixed-ligand complex is more stable than can be expected statistically. Kida pointed out that log $K_{\text{stab}}>0$ generally holds for such an equilibrium as is expressed in Eq. (1) by reason of the fact that both the electrostatic effect and the effect of the σ-covalency of the coordinate bond serve to promote the formation of a mixed-ligand complex.

The values of log K_{stab} are positive for all the systems except one, as may be seen in Table 7, but their values are quite different. It is important for us to investigate the reason for such different values, although it is not easy to do so at the present stage because of the insufficiency of data of this kind. The question whether or not the promotive formation of a mixed-ligand complex depends upon its stabilization in bond energy will, however, be answered by the experimental study of the temperature dependence of log K. log K is expressed as follows:[13]

$$\log K = \frac{1}{2.30\boldsymbol{R}}\left(-\frac{\Delta H}{T} + \Delta S\right) \qquad (3)$$
$$\Delta S = \Delta S_r + \Delta S_s$$

where ΔS_s is the entropy term of log $K_{\text{stat}}=\Delta S_s/2.30\boldsymbol{R}=0.60$ concerning the statistical distribution among the three complexes in Eq. (1) and where ΔS_r is designated as the summation of all the other unknown entropy terms. The error inherent in the ESR method of determining the K values may be somewhat larger than in the optical absorption method, mainly because of the assumed proportionality between the molar ratio of the three complexes and the ratio of the integrated intensities of the corresponding resolved Gaussian curves and because of the troublesome nature of the Gaussian analysis itself. Accordingly, it seems reasonable that the errors, which are ± 0.04 in Tables 1 and 2, were increased properly as much as about twofold for System I–III and about fourfold for System I–IV in Table 7. These increased errors, however, are, after all, counterbalanced from the point of view of the temperature dependence of log$K$ because of the very low temperature at which the K values are determined by the ESR method.

The thermodynamic constants were derived from the data in Table 7; they are listed in Table 8. The results in Table 8 indicate that the entropy change plays a main role in governing the equilibrium for all the systems. It is, furthermore, an interesting finding that the entropy values are almost constant for these systems, any one of which is concerned with ethylenediamine (as A in Eq. (1)) and amino acid (as B). On the other hand, the ΔG°_{293} values of the three systems are different from each other, and the enthalpy terms, whose values were different, are considered to be responsible for the differences in the value of ΔG°_{293}. Since the enthalpy term is related to the bond energies, the above-mentioned fact is consistent with Kida's proposal that the promotive formation of a mixed-ligand complex depends upon the electrostatic effect and also upon the effect of the σ-covalency of the coordinate bond. The enthalpy changes listed in Table 8 are comparatively small, especially for System I–III. This finding agrees with the ESR result already reported in a previous paper; the Cu–A and Cu–B bonds in Eq. (1) become close to each other in bond strength in the mixed-ligand complex, and there is an accompanying internal compensation for the bond energies.[11] A further study of the relations between these thermodynamic functions and the kinds of mixed-ligand complexes, or the other physico-chemical properties of the complexes, is now in progress. It is clear that all these data are fundamentally important for the structural estimation of the metalloenzyme-substrate complexes and for understanding their reaction mechanisms.

Table 8. Thermodynamic constants

		System$^{a)}$		
		I–II	I–III	I–IV
ΔG^{0}_{293}	(kcal/mol)	-1.93 ± 0.03	-1.05 ± 0.06	-0.19 ± 0.04
ΔH	(kcal/mol)	-0.86 ± 0.58	0.01 ± 0.20	1.20 ± 0.31
ΔS	(e.u.)	3.65 ± 0.21	3.62 ± 0.09	4.12 ± 1.20
ΔS_r	(e.u.)	0.89 ± 0.21	0.86 ± 0.09	1.36 ± 1.20

a) The systems are the ones referred to in Table 7.

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[13] S. Bruckeinstein and L. D. Pettit, *J. Amer. Chem. Soc.*, **88**, 4790 (1966).