The Coordination Bonding and Stability of the 1 : 1 Complexes of Copper(II) with Various Bidentate Ligands in Aqueous-methanolic Solutions

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ESR and spectrophotometric studies have been made of a number of 1 : 1 complexes of copper(II) with ethylenediamine, its analogues, and amino acids in aqueous-methanolic solutions. It has been shown that the complexes in the solutions are characteristic of copper(II) ions with a normal tetragonal environment and that their metal-ligand bondings are intermediate in the degree of covalency between those of hydrated cupric ions and the corresponding 1 : 2 complexes. The disproportionation constants and their temperature dependences, determined for the 1 : 1 complexes by the ESR and spectrophotometric methods, have been discussed, with particular empahsis on the fact that those values are in fair agreement with those derived from the step-by-step formation constants and the thermodynamic data obtained in aqueous solutions in the literature.

It is a very interesting problem in coordination chemistry to study the bonding character and stability of the 1 : 1 complexes of copper(II) with various bidentate ligands in aqueous solutions, sinec the 1 : 1 complexes can be regarded as intermediates in the formation of the 1 : 2 complexes. This problem is also of importance in estimating the reaction mechanisms of various metal-ion-catalyzed-reactions in organic, inorganic, and biological chemistries.[1–4] There have been almost no other works on the physical properties of the 1 : 1 complexes in solution but the one reported by Lewis *et al.*; they interpreted the ^{17}O NMR and ESR results of aqueous solutions of cupric salts and of 1 : 1 and 1 : 2 complexes of copper(II) with ethylenediamine in terms of molecular orbitals.[5]

The purpose of the present paper is to investigate the metal-ligand bondings of the 1 : 1 complexes of copper(II) with ethylenediamine, its analogues, and amino acids in aqueous-methanolic solutions, to compare them with those of cupric ions and the 1 : 2 complexes using the ESR and spectrophotometric methods, and furthermore, to discuss the stability of the 1 : 1 complexes in solution.

Experimental

Materials. The 1 : 1 complexes of copper(II) with bidentate ligands were produced according to equilibrium by mixing cupric ions and the 1 : 2 complexes in solution, as will be described in detail later. $Cu(ClO_4)_2 \cdot 6H_2O$ was used as the source of the cupric ions. The 1 : 2 complexes employed here, which had been prepared and purified in a previous work,[6] were $[Cu(en)_2]\cdot(ClO_4)_2$, $[Cu(dmen)_2]\cdot(ClO_4)_2$, $[Cu(deen)_2]\cdot(ClO_4)_2$, $[Cu(tn)_2]\cdot(ClO_4)_2$, [Cu(L-ala)₂], [Cu(L-ser)₂], and $[Cu(\beta\text{-ala})_2]\cdot 6H_2O$, where en, dmen, deen, tn, L-ala, L-ser, and β-ala are ethylenediamine, *N,N*-dimethylethylenediamine, *N,N*-diethylethylenediamine, trimethylenediamine, the anions of L-alanine, L-serine, and β-alanine respectively. The $(0.970\pm0.005)\times10^{-2}$ mol/l solution of the cupric ions and the 1.000×10^{-2} mol/l solutions of the 1 : 2 complexes were prepared using an equivolume mixture of water and methanol as the solvent; the concentration of cupric ions was checked by a usual colorimetric determination, using sodium diethyldithiocarbamate.[7]

Measurements. The sample solutions used for the ESR and spectrophotometric measurements were mixtures of the above-mentioned solution of cupric ion and any of the above-described solutions of the 1 : 2 complexes at various volume ratios. The ESR spectra were measured at the temperature of liquid nitrogen with a Hitachi 771 X-band ESR spectrometer. The measurements of the visible absorption spectra were carried out at room temperature with a Hitachi EPS-3T spectrophotometer, using 1-cm quartz cells.

Results and Discussion

When a cupric salt and a stable 1 : 2 complex of copper(II) with a bidentate ligand, A, are dissolved in an aqueous solvent, the following equilibrium is generally established in the solution (with charge and hydrated water molecules omitted):

$$Cu + CuA_2 \rightleftarrows 2CuA \qquad (1)$$

$$K = \frac{[CuA]^2}{[Cu][CuA_2]} \qquad (2)$$

where CuA represents a 1 : 1 complex. The relative amounts of the three species in the solution, therefore, vary according to the *K* value.

The X-band ESR spectra for the systems containing the 1 : 1 complexes of copper(II) with ethylenediamine and L-alanine are shown in Figs, 1 and 2 as typical ESR spectra in this work; the other systems showed almost the same spectral behavior. The ESR line shapes observed for the randomly-oriented and magnetically-diluted samples of copper(II) complexes have been investigated in some detail.[8] Accordingly,

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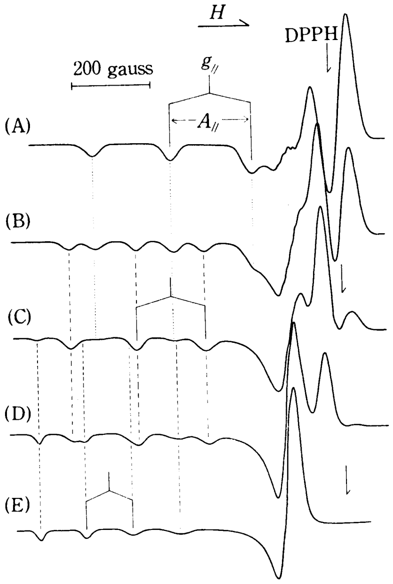

Fig. 1. The X-band ESR spectra of the mixtures of $Cu(ClO_4)_2 \cdot 6H_2O$ and $[Cu(en)_2] \cdot (ClO_4)_2$ in the following molar ratios (measured at 77K, total concentration of Cu(II) in each solution: 1×10^{-2} M, Solvent: an equivolume mixture of water and methanol).

(A) 0 : 1, (B) 1 : 3, (C) 1 : 1, (D) 3 : 1, (E) 1 : 0.

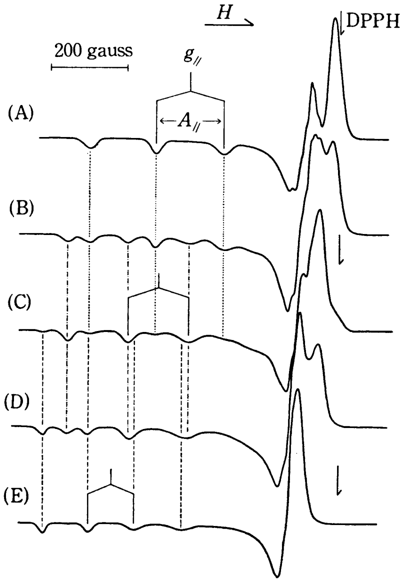

Fig. 2. The X-band ESR spectra of the mixtures of $Cu(ClO_4)_2 \cdot 6H_2O$ and $[Cu(L\text{-}ala)_2]$ in the following molar ratios (measured at 77K, total concentration of Cu(II) in each solution: 1×10^{-2} M, Solvent: an equivolume mixture of water and methanol).

(A) 0 : 1, (B) 1 : 3, (C) 1 : 1, (D) 3 : 1, (E) 1 : 0.

it is clear that all the ESR spectra observed for the mixtures of the cupric salt solution and any of the 1 : 2 complex solutions are made up of the superposition of three different spectra, as Figs. 1 and 2 show. The several vertical dotted lines in these figures clearly point out that two of the three spectra are due to Cu and CuA_2, and the third spectrum, to CuA; there are not more than these three species in any sample solution, and the three species may coexist at equillbrium. It has also been shown that all the ESR spectra of the

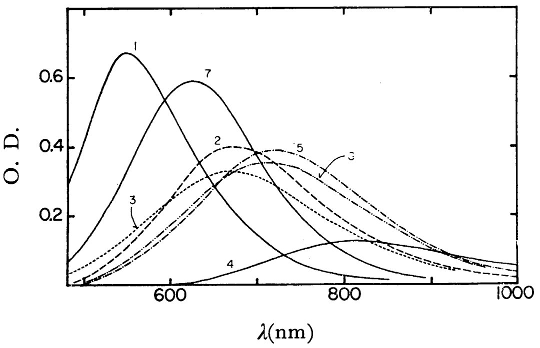

Fig. 3. The visible absorption spectra of the following complex species at room temperature (total concentration of Cu(II) in each solution: 1.00×10^{-2} M, Solvent: an equivolume mixture of water and methanol)

(1) $[Cu(en)_2] \cdot (ClO_4)_2$, (2) $[Cu(en)_2] \cdot (ClO_4)_2$, (2) $[Cu(en)_2] \cdot (ClO_4)_2 + Cu(ClO_4)_2$ (molar ratio of 1 : 1), (3) calculated spectrum of $[Cu(en)(OH_2)_2]^{2+}$, (4) $Cu(ClO_4)_2$, (5) $[Cu(L\text{-}ala)_2] + Cu(ClO_4)_2$ (molar ratio of 1 : 1), (6) calculated spectrum of $[Cu(L\text{-}ala)(OH_2)_2]^+$, (7) $[Cu(L\text{-}ala)_2]$.

CuA_2 species employed in this work are of an axially-symmetrical type.[9,10] The computer simulation of ESR line shapes, furthermore, has revealed that any of the ESR spectra of Cu, CuA, and CuA_2 (A=en) in frozen aqueous solutions are characteristic of cupric ions with an axially-symmetric *g* tensor.[5] It can reasonably be concluded, from all the observed ESR line shapes in this work, that each of the CuA species also has a normal tetragonal copper(II) environment. The $g_{//}$ and $|A_{//}|$ values analyzed for all the species are listed in Table 1.

The visible absorption spectra of the same sample solutions as in Figs. 1 and 2 are shown in Fig. 3; they are typical of this work. The visible absorption spectrum of CuA can be obtained using the *K* value in Eq. (2) and the spectral data of Cu and CuA_2. A spectrophotometric method for determining the *K* value will be described later. Some of the analyzed data are listed in Table 1. It can be seen from this table the wavelength of the maximum absorption of CuA appears almost in the middle between those of Cu and CuA_2; this fact suggests that the ligand-field energies of CuA may be intermediate between those of Cu and CuA_2. Furthermore, concerning the dipole strength of the visible absorption transition, *D*, we found that CuA is intermediate in the *D* value between Cu and CuA_2. It has generally been accepted that the intensity of the visible absorption spectrum in a copper(II) complex always increases as the symmetry of its ligand field decreases.[11,12] Accordingly, it seems probable that CuA is not much lower in the symmetry of the ligand field than are Cu and CuA_2. From the fact of an axially-symmetric *g* tensor of CuA, and from

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TABLE 1. EXPERIMENTAL DATA OF COPPER(II) COMPLEXES

Sample[a]	pH[b]	$g_{//}$	$\lvert A_{//}\rvert \times 10^4$ (cm^{-1})	Visible absorption maximum[c] λ(nm)	; ε	$D \times 10^3$ [d] (Å^2)	$k_{//}^2$ [e]
$Cu(OH_2)_4$	4.8	2.421	132	810	; 13	2.2	0.78
$Cu(en)_2$	8.0	2.204	209	554	; 66	8.5	0.54
$Cu(dmen)_2$	7.9	2.206	195	570	; 146	18.6	0.53
$Cu(deen)_2$	8.0	2.210	185	594	; 192	27.3	0.52
$Cu(tn)_2$	8.9	2.218	199	574	; 110	15.0	0.56
$Cu(\text{L-ala})_2$	7.9	2.262	181	622	; 58	7.7	0.62
$Cu(\text{L-ser})_2$	7.8	2.264	179	628	; 52	7.1	0.63
$Cu(\beta\text{-ala})_2$	8.7	2.282	141	630	; 59	7.7	0.66
$Cu(en)(OH_2)_2$		2.281	185	682(666)	; 40(32)	5.6(5.4)	0.62
$Cu(dmen)(OH_2)_2$		2.286	179	693(680)	; 59(56)	8.7(8.9)	0.62
$Cu(dmen)(OH_2)_2$		2.268	177	692(690)	; 88(83)	13.9(14.2)	0.58
$Cu(tn)(OH_2)_2$		2.283	181	664(656)	; 48(47)	6.7(6.8)	0.64
$Cu(\text{L-ala})(OH_2)_2$		2.320	167	718(705)	; 40(36)	5.9(5.6)	0.68
$Cu(\text{L-ser})(OH_2)_2$		2.321	166	716(710)	; 38(33)	5.5(5.2)	0.68
$Cu(\beta\text{-ala})(OH_2)_2$		2.322	160	728(726)	; 46(38)	6.3(5.9)	0.67

a) The samples represent the solutions of the complexes listed in this table, which are expressed with charge omitted, where an equivolume mixture of water and methanol was used as the solvent.

b) The pH at 25°C in a concentration of 0.01 M.

c) The values in parentheses are the data for the equimolar mixture of cupric ions and the 1 : 2 complexes in the above-mentioned solvent.

d) D represents the dipole strength of visible absorption transition;

$$D = 3.99 \times 10^{-20} \int \frac{\varepsilon_\sigma}{\sigma} d\sigma \quad (cm^2)$$

where σ expresses the wave number. The values in parentheses mean the same as given in the above footnote (b).

e) See the text.

the fact that CuA is intermediate in the values of D and of ligand field energies between Cu and CuA_2, it can be concluded that the ligand field of CuA is of an axial symmetry to almost the same degree as those of Cu and CuA_2. This conclusion, which is unexpected in view of the fact that the coordination symmetry of CuA is apparently less than tetragonal, agrees with the previously-reported suggestion that the symmetry of a ligand field is kept in as high a degree as possible for the copper(II) complexes in solution.[6]

The $g_{//}$ and $\lvert A_{//}\rvert$ values of CuA are intermediate between those of Cu and CuA_2, although CuA is somewhat closer to CuA_2 than to Cu in these values. The $g_{//}$ value is a good parameter for estimating the the degree of covalency of the metal-ligand bondings in planar copper(II) complexes; generally, the metal-ligand bondings become more covalent as the $g_{//}$ values increase.[13] The covalency of the metal-ligand bonding of CuA, therefore, is intermediate in degree between those of Cu and CuA_2. The same result can be derived from a consideration of the orbital reduction tion factors, one of which, $k_{//}^2$, is expressed in the following equation:

$$g_{//} - 2 = \frac{8\lambda_0 k_{//}^2}{\Delta E} \tag{3}$$

where λ_0 is the spin-orbit coupling constant for the free cupric ion and where $\Delta E = E_{x^2-y^2} - E_{xy}$. This $k_{//}^2$ value also has been considered to be an approximate parameter for expressing the degree of covalency of metal-ligand bondings for a series of square-planar copper(II) complexes structurally similar to each other.[14–16] The relative values of $k_{//}^2$ were calculated for all the copper(II) complexes dealt with here, using the energy value at the absorption peak as ΔE for convenience; they are listed in Table 1. It is clearly shown in this table that CuA is intermediate in the $k_{//}^2$ value between Cu and CuA_2. The findings that the metal-ligand bonding of CuA is intermediate in the degree of covalency between those of Cu and CuA_2, and that CuA is of a nearly tetragonal symmetry in the copper(II) ion environment, mean that the Cu-OH_2 bond in the molecular plane of CuA becomes stronger than that of Cu and the Cu–A bond of CuA, weaker than that of CuA_2, and, consequently, that, in CuA, the bond strength of in-plane Cu–OH_2 is almost equal to that of Cu–A.

When the step-by-step formation constants of K_1 and K_2 are expressed as follows (with charge and hydrated water molecules omitted):

$$Cu + A \rightleftharpoons CuA \qquad K_1 = \frac{[CuA]}{[Cu][A]} \tag{4}$$

$$CuA + A \rightleftharpoons CuA_2 \qquad K_2 = \frac{[CuA_2]}{[CuA][A]} \tag{5}$$

the following general equations can be set up, using K in Eq. (2):

$$\log K = \log K_1 - \log K_2 \tag{6}$$

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TABLE 2. RESULTS OF THE OPTICAL ABSORPTION MEASUREMENTS[a] FOR THE SYSTEM: $Cu+Cu(en)_2$[b]

			λ(nm)			
			500	510	520	530
		$Cu(en)_2$: Cu				
D'	(I)	1 : 0.97	0.072	0.090	0.108	0.127
	(II)	2 : 0.97	0.168	0.202	0.237	0.264
	(III)	3 : 0.97	0.228	0.273	0.315	0.349
ε_p			42.3	50.3	57.2	62.6
y	(I)		−28.8	−33.3	−36.7	−38.4
	(II)		−35.3	−41.2	−44.6	−47.4
	(III)		$-36._8$	−43.0	−47.0	−49.7
$\Delta\varepsilon$	(i)	from (I) and (II)	−39.4	−46.9	−49.2	−53.8
	(ii)	from (I) and (III)	$-39._1$	−46.0	−50.0	−53.3
	(iii)	from (II) and (III)	$-39._0$	−45.5	−50.6	−53.0
P	(i)		−1.17	-1.22_6	-1.15_0	-1.21_8
	(ii)		−1.17	-1.19_3	-1.17_3	-1.20_3
	(iii)		−1.16	-1.14_9	-1.21_9	-1.18_2
K	(i)		$26._5$	$21._7$	$30._7$	$22._4$
	(ii)		27	$24._7$	$27._1$	$23._7$
	(iii)		29	$30._9$	$22._3$	$26._0$
				Mean value:	$K=26.1\pm0.7$	

a) At 25°C, Solvent: an equivolume mixture of water and methanol.

b) The system of $Cu+Cu(en)_2$ represents the mixture of $Cu(ClO_4)_2$ and $[Cu(en)_2]\cdot(ClO_4)_2$ in the above-described solvent.

TABLE 3. RESULTS OF THE OPTICAL ABSORPTION MEASUREMENTS[a] FOR THE SYSTEM: $Cu+Cu(L\text{-}ala)_2$[b]

			λ(nm)			
			510	520	530	540
		$Cu(L\text{-}ala)_2$: Cu				
D'	(I)	1 : 0.97	0.025	0.035	0.046	0.059
	(II)	2 : 0.97	0.063	0.083	0.105	0.130
	(III)	3 : 0.97	0.085	0.111	0.141	0.172
ε_p	(I)		15.5	21.1	25.2	30.6
y[c]			15.5	20.1	25.2	30.6
	(II)		−12.5	−15.8	−19.5	−22.3
	(III)		−12.9	−16.4	−19.8	−23.3
$\Delta\varepsilon$	(i)	from (I) and (II)	−13.0	−16.6	−20.7	−23.0
	(ii)	from (I) and (III)	−13.2	−17.0	−20.4	−23.9
	(iii)	from (II) and (III)	−13.4	−17.2	−20.2	−24.8
P	(i)		-1.05_0	-1.06_5	-1.08_2	−1.08
	(ii)		-1.06_2	-1.08_1	-1.06_9	-1.09_1
	(iii)		-1.10_5	-1.13_2	-1.04_1	-1.11_6
K	(i)		84	66	53	53
	(ii)		69	53	62	48
	(iii)		42	34	102	39
				Mean value:	$K=59\pm5$	

a) At 25°C, Solvent: an equivolume mixture of water and methanol.

b) The system of $Cu+Cu(L\text{-}ala)_2$ represents the mixture of $Cu(ClO_4)_2$ and $[Cu(L\text{-}ala)_2]$ in the above-described solvent.

c) All the y values were calculated from Eq. (10), on the assumption that all the D' values have no error (the actual experimental error of D' is ±0.001).

Table 4. The values of log K

No.	System[a]	pH[b]	Solvent: water-methanol(1 : 1)[c]		Solvent: water	
			Spectrophotometric method (25°C)	ESR method (−50—−100°C)	Calcd[d] (25°C)	Temperature dependence[e] ($\log K_{25}-\log K_0$)
I	$Cu+Cu(en)_2$	5.7	1.42 ± 0.02	1.61 ± 0.05	1.43 ± 0.03	-0.03 ± 0.01
II	$Cu+Cu(dmen)_2$	5.6	2.10 ± 0.03	2.72 ± 0.10	2.04 ± 0.39	(0.05)
III	$Cu+Cu(deen)_2$	5.9	1.99 ± 0.05	2.86 ± 0.12	2.62	
IV	$Cu+Cu(tn)_2$	6.3	2.26 ± 0.05	2.66 ± 0.10	2.65 ± 0.04	-0.03 ± 0.01
V	$Cu+Cu$(L-ala)	5.4	1.77 ± 0.04	1.43 ± 0.05	1.59 ± 0.05	-0.06 ± 0.01
VI	$Cu+Cu$(L-ser)$_2$	5.3	1.50 ± 0.03	1.36 ± 0.07	(1.60)[f]	(0.06)[f]
VII	$Cu+Cu(\beta\text{-ala})_2$	5.8	1.36 ± 0.04	1.40 ± 0.07	1.76 ± 0.06	0.13

a) The system means the mixtures of cupric ions and the 1 : 2 complexes (with charge and hydrated water molecules omitted).
b) The pH at 25°C of the equivolume mixture of the 0.01 M aqueous-methanolic solutions of the two species in each system.
c) An equivolume mixture of water and methanol. d) The values of log K in aqueous solution were calculated from Eq. (6) using the stepwise formation constants in the literature which determined in aqueous solution chiefly by the glass electrode method.[19,20] The values with errors express the means of two or more data. e) The value of ($\log K_{25}-\log K_0$) was used as a measure of the temperature dependence of log K in aqueous solution, where K_t represents K at t°C. The values with errors express the means of two or more data. f) Since the data for this system have not been reported, the values determined for the system $Cu+Cu$(L-thr)$_2$ were cited for reference, where L-thr represents the anion of L-threonine.

$$\log K = \frac{1}{2.30R}\left\{-\frac{(\Delta H_1-\Delta H_2)}{T}+(\Delta S_1-\Delta S_2)\right\} \tag{7}$$

where the symbols written in Eqs. (6) and (7) have their usual meanings. The values of log K were determined by the usual spectrophotometric method.[17]

When we represent the total concentrations of CuA_2 and Cu with xc and c respectively, and the concentration of CuA, with u, the equilibrium constant in Eq. (2) can be written by:

$$K = \frac{4u^2}{(xc-u)(c-u)} \tag{8}$$

On the other hand, the observed optical density, D', at a wavelength where the absorption of Cu is negligible is as follows:

$$D' = \varepsilon_p(xc-u) + 2\varepsilon_m u \tag{9}$$

where ε_p and ε_m mean the extinction coefficients of CuA_2 and CuA respectively. Furthermore, y and $\Delta\varepsilon$ were defined as follows:

$$y = \frac{D'-\varepsilon_p xc}{c} = (2\varepsilon_m-\varepsilon_p)\cdot\frac{c}{u} = \Delta\varepsilon\cdot\frac{u}{c} \tag{10}$$

From Eqs. (8) and (10), we obtain;

$$y^2 + P\cdot(1+x)\cdot y\cdot\Delta\varepsilon - P\cdot x\cdot\Delta\varepsilon^2 = 0 \tag{11}$$

where $P=K/(4-K)$. When two numerical sets of the x and y values at a certain wavelength are introduced into Eq. (11), we can find the values of $\Delta\varepsilon$ and P, from which the value of K can then be determined. The observed optical densities and the calculated values of y, $\Delta\varepsilon$, P, and K for the same systems as in Fig. 3 are listed in Tables 2 and 3. All the values of log K determined by this spectrophotometric method and by the previously-described ESR method[18] are listed in Table 4, together with the values of log K and their temperature dependences, which were calculated from Eqs. (6) and (7) using the step-by-step formation constants and the thermodynamic constants obtained in aqueous solutions by many investigators.[19,20]

It is clearly shown in Table 4 that the values of log K listed in the third, fourth, and fifth columns of the table are comparable to each other. All these values, moreover, are larger than the value of log K expected statistically, 0.60;[21] this means that there exist certain factors which promote the formation of the 1 : 1 complexes.[18,22–24] It seems likely that appreciably-accurate values of log K can be obtained by the ESR method, since all the magnetic parameters of CuA are intermediate in magnitude between those of Cu and CuA_2, since essential errors in estimating the concentrations of the three species are possibly cancelled out in Eq. (2).[18] However, the temperature at which the values of log K were determined by this ESR method is uncertain, although it is definitely a temperature between −50 and −100°C.[18] The temperature dependences of log K for all the systems in aqueous-methanolic solutions can be estimated by comparing the values of log K in the third and fourth columns of Table 4. In most systems, the temperature dependences in aqueous-methanolic solutions are in fair agreement with those in aqueous solutions. In System II, however, the temperature dependence of log K determined in this work is different

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[20] J. J. Christensen and R. M. Izatt, "Handbook of Metal Ligand Heats and Related Thermodynamic Quantities," Marcel Dekker, New York (1970).

[21] The value of 0.60 can be formally explained on the following scheme, assuming that there are $4n$ particles of Cu and A respectively in solution and A is bonded to either Cu or CuA with the same probability.
$[4n\,Cu+4n\,A]\rightarrow[(2n\,Cu, 2n\,CuA)+2n\,A]\rightarrow[n\,Cu, 2n\,CuA, n\,CuA_2]$
Accordingly, $\log K=\log[Cu][CuA_2]=\log n\times n=\log 4=0.60$.

[22] R. De Witt and J. I. Watters, *J. Amer. Chem. Soc.*, **76**, 3810 (1954); J. I. Watters, A. Aaron, and J. Mason, *ibid.*, **75**, 5212 (1953); J. I. Watters and E. D. Longham, *ibid.*, **75**, 4819 (1953).

[23] S. Kida, This Bulletin, **29**, 805 (1956).

[24] S. Kida, *ibid.*, **34**, 962 (1961).

in tendency from that obtained in aqueous solutions, although this result may not be accurate because of insufficient thermodynamic data on aqueous solutions for this system. The values of log K at 25°C listed in the third and fifth columns of Table 4 are somewhat different for the systems having relatively less stable 1 : 2 complexes. These differences may be due to the different solvent used, since the solvent effect on the complexes becomes more profound as they are less stable. Systems I—IV are those diamines, and Systems V—VII, those of amino acids. It is also shown in Table 4 that, in the former systems, the values of log K increase with a rise in the temperature, while in the latter systems the values decrease. The thermodynamic constants derived from these data are listed in Table 5. It is well known that, in complex formation, the nitrogen donors are softer than the oxygen donors and that both ΔH and ΔS are markedly lower for the formation of complexes by nitrogen than oxygen donors.[25] For both copper(II) complexes of ethylenediamine and L-alanine, the difference between ΔH_1 and ΔH_2 is quite small in magnitude, but the difference between ΔS_1 and ΔS_2 is markedly larger for the L-alanine complex than for the ethylenedimaine complexes; for the latter complex, $\Delta S_2=0$ and ΔS_1 is much smaller in magnitude than ΔS_1 and ΔS_2 for the former complex. Accordingly, the entropy term is more important in stabilizing the 1 : 1 complexes for amino acids than for diamines, as is clearly demonstrated in Table 5.

TABLE 5. THERMODYNAMIC CONSTANTS FOR $Cu + CuA_2 \rightleftharpoons 2CuA$[a)]

No.	System	(kcal/mol) ΔH	ΔS (e. u.)
I	$Cu+Cu(en)_2$	-0.51 ± 0.24 (-0.34 ± 0.10)	4.8 ± 0.7 (5.6 ± 0.3)
II	$Cu+Cu(dmen)_2$	-1.68 ± 0.43	4.0 ± 1.3
III	$Cu+Cu(deen)_2$	-2.35 ± 0.60	1.2 ± 1.7
IV	$Cu+Cu(tn)_2$	-1.08 ± 0.54	6.7 ± 1.6
V	Cu+Cu(L-ala)$_2$	0.92 ± 1.27 (0.9)	11.2 ± 1.0 (9.9)
VI	Cu+Cu(L-ser)$_2$	0.38 ± 0.35	8.1 ± 1.0
VII	Cu+Cu(β-ala)$_2$	-0.11 ± 0.46	5.9 ± 1.3

a) The solvent used is an equivolume mixture of water and methanol. The temperature at which the K values are determined by the ESR method was assumed to be −75°C. The values in parentheses in the table are the ones derived from the data in aqueous solution in the literature.[19,20)]

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25) S. Ahrland, "Structure and Bonding," Vol. 5, ed. by C. K. Jørgensen, R. S. Nyholm, and R. J. P. Williams, Springer-Verlag, Berlin (1968), p. 118.