Studies of the Coordination Bonding and Stability of the Mixed-ligand Complexes of Copper(II)

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In recent years, many studies of the stability of mixed-ligand complexes have been carried out; the importance of the chemical behavior of the complexes have received increasing attention from the viewpoint of its relationship to fundamental concepts in inorganic and biological chemistry.[1–3] More quantitative studies, however, seem to be necessary for determining definitely the factors governing the mixed-ligand complex formation.[3] We wish to report here on our new results concerning the coordination bonding and stability for the mixed-ligand complex written in the following equilibrium (the results were obtained by the use of ESR and optical absorption techniques):

$$\mathrm{CuA_2 + CuB_2 \rightleftharpoons 2\,CuAB} \qquad (1)$$

$$K = \frac{[\mathrm{CuAB}]^2}{[\mathrm{CuA_2}]\,[\mathrm{CuB_2}]} \qquad (2)$$

Here, two different bidentate ligands of ethylenediamine, its alkyl derivatives, trimethylenediamine, and various amino acids are represented as A and B, and an equivolume mixture of water and methanol was used as the solvent.

The observed ESR line shapes showed that the symmetry of the ligand field of all the mixed-ligand complexes employed is as axial as that of the parent complexes. It was found that the $g_{//}$ and $g_{\perp}$ values of almost all the mixed-ligand complexes are intermediate between those of the corresponding two parent complexes, as is shown in Fig. 1, for example, with regard to the $g_{//}$ value; furthermore, the wavelengths and intensities of the visible absorption maximum of the mixed-ligand complexes are intermediate. It may be concluded from these experimental facts that the mixed-ligand complexes are intermediate in the degree of covalency of the coordinate bond between the corresponding two parent complexes.[4]

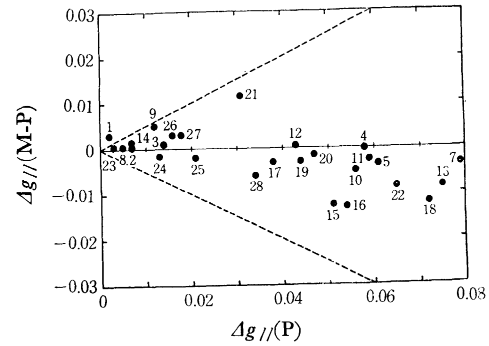

Fig. 1. A plot of $\Delta g_{//}$(M-P) against $\Delta g_{//}$(P) for 28 mixed ligand complexes.
$\Delta g_{//}(\mathrm{M\text{-}P}) = g_{//}{}^{\mathrm{M}} - (1/2)(g_{//}{}^{\mathrm{P_1}} + g_{//}{}^{\mathrm{P_2}})$
$\Delta g_{//}(\mathrm{P}) = |g_{//}{}^{\mathrm{P_1}} - g_{//}{}^{\mathrm{P_2}}|$
where $g_{//}{}^{\mathrm{M}}$, $g_{//}{}^{\mathrm{P_1}}$, and $g_{//}{}^{\mathrm{P_2}}$ are the $g_{//}$ values of a mixed ligand complex and its two parent complexes, $\mathrm{P_1}$ and $\mathrm{P_2}$, respectively.

The K values and the thermodynamic constants were determined for several equilibrium systems (A: ethylenediamine, B; amino acid) in order to estimate the factors governing the equilibrium; the data are listed in Tables 1 and 2. These results indicate that the entropy term plays a main role in determining the equilibrium, but that the differences in the K values are due to small differences in the enthalpy change. The fact that the enthalpy changes are small seems to be in agreement with the average of the Cu-A and Cu-B bond strengths in the mixed-ligand complexes, as has been mentioned above.

The details will soon be published elsewhere.

Table 1. The value of log K[a)]

Temperature (°C)	System[b)] I	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
ca. −100[c)]		0.79±0.10	−0.45±0.15

a) The K values at 20 and 50°C were determined spectrophotometrically according to the Kida's method,[2)] and the K values at *ca.* −100°C were determined from the X-band ESR spectra measured at 77°K by resolving the absorption lines into three components.

b) I: A=en, B=L-Ala, II: A=en, B=β-Ala, III: A=en, B=dmg (dmg: *N,N*-dimethylgylcine anion, other abbreviations are the ones ordinarily used).

c) the assumed freezing point.

Table 2. Thermodynamic constants

	System I	II	III
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	1.02±0.31
ΔS (e.u.)	3.65±0.21	3.62±0.09	4.12±1.20

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