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An ESR Study of the 1 : 2 Complexes of Copper(II) with Optically-active and Racemic α-Amino Acids

Hiroshi Yokoi, Mitsuru Sai, and Taro Isobe

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai

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Any of the crystal structures of the metal complexes of amino acids are unpredictably unique because of their characteristic hydrogen-bonding behavior.[1,2] Various properties of the complexes in crystal have been studied by the IR,[3-6] visible absorption,[6,7] and ESR[8] methods. Special attention has been given to stereospecific effects in complexes of metals with optically-active ligands.[9] The purpose of this paper is briefly to communicate the ESR results of the 1 : 2 complexes of copper(II) with various optically-active and racemic α-amino acids in various states.

Experimental

Materials. The copper(II) complexes employed here are listed in Table 1, together with their abbreviations. They all were prepared according to the usual methods,[6,10] using commercial G.R.-grade α-amino acids, and were recrystallized from water. [Cu(L-Ala)$_2$] and [Cu(L-Val)$_2$] were prepared by heating the corresponding hydrates *in vacuo* at about 160°C. All the complexes were identified by elemental analysis.

Measurements. The X-band and K-band ESR spectra of the complexes were measured in a polycrystalline state at room temperature and in a frozen solution at the temperature of liquid nitrogen with a Hitachi ESR spectrometer, Model MES-4001. The sample solutions contained the complexes in concentrations of 10^{-3}—10^{-2}M, where an equivolume mixture of water and methanol was used as the solvent. The visible absorption spectra of the complexes in a polycrystalline state were measured by the so-called opal glass method with a Cary model 14 spectrometer.[11]

TABLE 1. EXPERIMENTAL DATA

Ligand	Copper (II) complex[a]	Polycrystals[b]				Frozen solution[c]			
		g_1	g_2	g_3	λ_{max}[d] (nm)	$g_{//}$[e]	$g_{\perp}$[f]	$\lvert A_{//}\rvert$[g] × 10^4 (cm^{-1})	λ_{max}[h] (nm)
L-Alanine	[Cu(L-Ala)$_2$]	2.059	2.107	2.198	590	2.264	2.056	178.3	620
DL-Alanine	[Cu(DL-Ala)$_2$]·H_2O	2.053	2.122	2.180	580	2.264	2.056	178.5	620
	[Cu(DL-Ala)$_2$]	2.054	2.100	2.202	580				
L-Valine	[Cu(L-Val)$_2$]·H_2O	2.059		2.243	617	2.269	2.055	171.9	615
	[Cu(L-Val)$_2$]	2.054		2.237	622				
DL-Valine	[Cu(DL-Val)$_2$]	2.056	2.105	2.202	603	2.268	2.056	174.9	615
L-Serine	[Cu(L-Ser)$_2$]	2.056	2.157		603	2.266	2.057	176.2	623
DL-Serine	[Cu(DL-Ser)$_2$]	2.058	2.111	2.208	615	2.264	2.056	179.4	623
L-Proline	[Cu(L-Pro)$_2$]·$2H_2O$	2.059	2.158		610	2.261	2.058	188.0	610
DL-Proline	[Cu(DL-Pro)$_2$]·$2H_2O$	2.065[i]		2.190[i]	605	2.266	2.056	178.7	610

a) The abbreviations of L-Ala *etc.* represent the anions of ligands.
b) The numbers written between neighboring *g* columns express the *g* values in both of the column.
c) The $g_{//}$ and $A_{//}$ values were determined from the *X*-band ESR spectra measured in aqueous-methanolic (an equivolume mixture) solution at 77°K.
d) ±4 nm.
e) ±0.001.
f) The $g_{\perp}$ values were determined from the K-band ESR spectra, as an example in Fig. 2 shows.
g) ±0.5.
h) measured in aqueous solution at room temperature.
i) The *g* values were tentatively determined from the positions shown by arrows in Fig. 1 (10).

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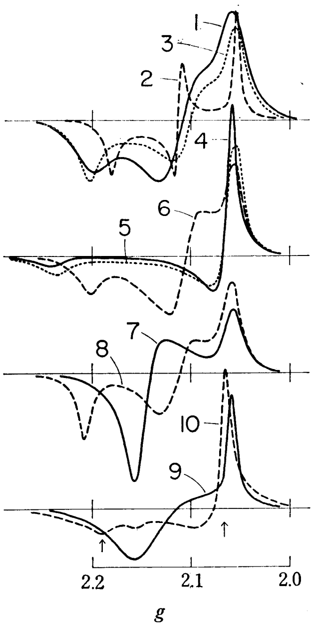

Fig. 1. Powder K-band ESR spectra at room temperature. (1): [Cu(L-Ala)$_2$], (2): [Cu(DL-Ala)$_2$]·H_2O, (3): [Cu(DL-Ala)$_2$], (4): [Cu(L-Val)$_2$]·H_2O, (5): [Cu(L-Val)$_2$], (6): [Cu(DL-Val)$_2$], (7): [Cu(L-Ser)$_2$], (8): [Cu(DL-Ser)$_2$], (9): [Cu(L-Pro)$_2$]·$2H_2O$, (10): [Cu(DL-Pro)$_2$]·$2H_2O$.

Results and Discussion

Powder ESR Spectra. All the powder K-band ESR spectra are shown in Fig. 1; they were analyzed by the use of the approximation of Kneubühl.[12] The results are listed in Table 1, together with the visible absorption data. It has been suggested that there may be no such strong spin-exchange interactions as affect the *g* values in most crystals of the *trans* 1 : 2 complexes of copper (II) with amino acids.[8,13]

The ESR line shape of [Cu(DL-Ala)$_2$]·H_2O was quite different from that of [Cu(L-Ala)$_2$]. The dehydration of [Cu(DL-Ala)$_2$]·H_2O caused a drastic change in the ESR spectrum; the resulting spectrum resembled that of [Cu(L-Ala)$_2$]. This fact indicates that the water molecule of [Cu(DL-Ala)$_2$]·H_2O in a crystal is influential in determining the copper(II)-ion environment. The ESR line shapes of [Cu(DL-Val)$_2$] and [Cu(DL-Ser)$_2$] were also similar to that of [Cu(L-Ala)$_2$]. Their optically-active isomers, however. were quite different in line shape from [Cu(L-Ala)$_2$], The spectra of both [Cu(L-Val)$_2$] and its hydrate, whose *g* values were almost the same, indicate an elongated-tetragonal copper(II)-ion environment; therefore, the water molecule of this hydrate is of little importance to the copper(II)-ion environment. On the other hand, [Cu(L-Ser)$_2$] showed a so-called reverse ESR spectrum ($g_{/\!/} < g_{\perp}$) as well as [Cu(L-Pro)$_2$]·$2H_2O$. [Cu(L-Ser)$_2$] is known to adopt a *cis*-configuration,[14] and it has been inferred from IR measurements that [Cu(L-Pro)$_2$]·$2H_2O$ also adopts a *cis*-geometry.[5] The crystal of [Cu(L-Ser)$_2$] is quite different from those of the other *trans* complexes in the packing of crystallographically non-equivalent molecular pairs,[1,8,14] and it seems likely that the reverse ESR spectrum is caused by a spin-exchange interaction which is effective on the crystal structure of the *cis* complex. In a word, all the above-mentioned experimental facts clearly indicate that a sensitive detection and investigation of the stereospecificity in a metal complex in a crystylline solid can be carried out by the ESR method.

Solution ESR Spectra. All the ESR line shapes observed for the complexes in a frozen aqueous-methanolic solution were quite similar to each other; this fact is in striking contrast with the results in a crystalline solid. The K-band ESR line shapes indicate especially clearly that the copper(II) ions are present in a tetragonal field, as the example shown in Fig. 2 shows. This behavior of the complexes in solution may be regarded as a general property of the planar copper (II) complexes.[15]

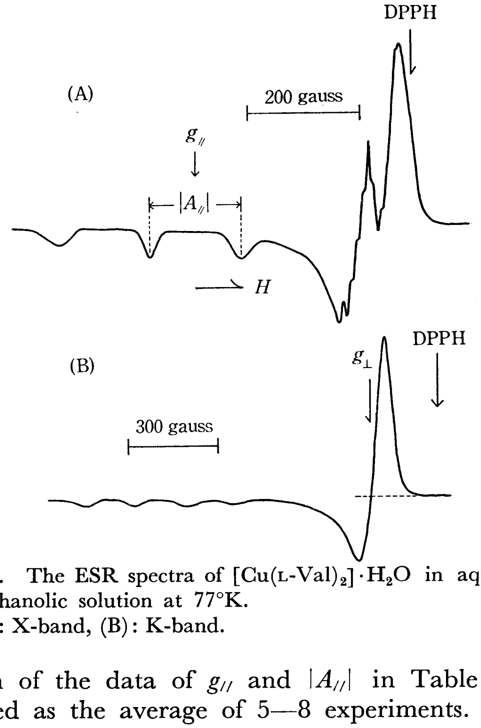

Fig. 2. The ESR spectra of [Cu(L-Val)$_2$]·H_2O in aqueous-methanolic solution at 77°K.
(A): X-band, (B): K-band.

Each of the data of $g_{/\!/}$ and $|A_{/\!/}|$ in Table 1 was obtained as the average of 5—8 experiments. These data clearly indicate that there is a small but significant difference in the copper(II)-ion environment between the optical isomers in frozen solutions. Interestingly, the ORD experiments for analogous samples in aqueous solutions showed that the conformation of the chelate ring influences the apical coordination of water molecules.[16] In this work, however, the observed difference between the isomers is too small to reveal what structural difference there is practically. A racemic copper(II) complex in solution is distributed among the three isomers, [Cu(L-A)$_2$], [Cu(D-A)$_2$], and [Cu(L-A)(D-A)],

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in the statistically-expected concentration ratio of 1 : 1 : 2,17) where A represents an α-amino acid anion. This fact indicates that the essential difference in any parameter between $[\mathrm{Cu(L\text{-}A)_2}]$ and $[\mathrm{Cu(L\text{-}A)(D\text{-}A)}]$ is larger than the observed one.

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