Spectral Properties of Mixed Ligand Copper(II) Complexes Containing L-α-Amino Acids

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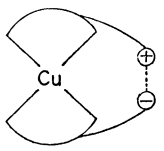
Absorption and circular dichroism (CD) spectral behaviors of ternary copper(II) complexes containing two L-α-amino acids or an L-α-amino acid and iminodiacetate (ida), 2,2′-bipyridine (bpy), 2-pyridinecarboxylate (pca), or 2,6-pyridinedicarboxylate (pdca), have been studied comparatively, and synthetic studies have given as crystals the mixed ligand complexes, [Cu(ida)(L-arg)]·$2H_2O$, [Cu(ida)(L-orn)]·$2H_2O$, [Cu(ida)(L-lys)]·$1/4H_2O$, [Cu(pdca)(L-arg)]·H_2O, and [Cu(pdca)(L-orn)]·$2.5H_2O$, where L-arg, L-orn, and L-lys denote L-arginine, L-ornithine, and L-lysine, respectively. The CD magnitudes of the systems Cu(ida)(L-arg), Cu(ida)(L-orn), and Cu(ida)(L-lys) were found to be enhanced appreciably as compared with the magnitudes estimated from the values for the corresponding binary systems. These ternary systems showed further magnitude enhancements in 50% aqueous ethanol. The enhanced magnitudes observed for Cu(L-glu)(L-arg), where L-glu is L-glutamate, were also intensified in 10, 20, and 50% aqueous ethanol, whereas they were weakened nearly to the estimated values in aqueous solutions with higher ionic strengths (μ=0.1 and 0.5($NaClO_4$)). These observations support the view that the pairs of ligands constituting the above ternary complexes are fixed around copper(II) by electrostatic ligand-ligand interactions between the oppositely charged side chains. Pyridine-containing ligands, bpy, pca, and pdca, in the ternary systems with L-α-amino acids affected the signs and the magnitudes of the CD spectra.

Mixed ligand complexes as potential biological models have been studied most extensively by the potentiometric method, which has made available valuable information about the stabilities and distributions of complex species in solution.[1,2] Because of the biological importance of copper, a great deal of attention has been paid to the ternary copper(II) complexes containing optically active amino acids and peptides, where circular dichroism (CD) has often proved to be a more direct and effective source of information.[3,4]

In our previous studies on the ternary copper(II) systems composed of α-amino acids and related compounds,[5,6] the synthetic and spectroscopic findings have been interpreted as supporting the existence of the intramolecular electrostatic ligand-ligand interactions between the oppositely charged side groups around the central copper(II) ion as tentatively shown in Scheme 1. Facile isolation of the corresponding



Scheme 1.

mixed ligand complexes implicated that such electrostatic bondings served as a driving force leading to the formation of mixed ligand complexes. While the ternary systems without the possibility of the ligand-ligand interactions exhibited the CD magnitudes equal to those estimated from the corresponding binary systems, most of the ternary systems expected to involve such interactions were accompanied by magnitude enhancements probably due to the structural rigidity.[5,6]

Martin and Prados[7] detected a CD magnitude enhancement and sign inversions for the systems Cu(2,2′-bipyridine)(L-phenylalanine) and Cu(2,2′-bipyridine)(L-alanine or L-leucine), respectively, and they ascribed the behaviors to the presence of the pyridine ring as a π-acceptor. On the other hand, Tsangaris and Martin[8] observed that the magnitudes were additive in the Cu(dipeptide) series.

Interests in the structural and spectral properties of the ternary systems and the demand for the relevant information prompted us to investigate the visible absorption and CD spectra of various ternary copper(II) systems containing two L-α-amino acids or an L-α-amino acid and iminodiacetate (ida), 2,2′-bipyridine (bpy), 2-pyridinecarboxylate (pca), or 2,6-pyridinedicarboxylate (pdca) under different conditions. We isolated for the present purpose several copper(II) complexes, Cu(A)(B), containing iminodiacetate or 2,6-pyridinedicarboxylate as ligand A and L-arginine (L-arg), L-ornithine (L-orn), or L-lysine (L-lys) as ligand B. The present paper describes the results obtained therefrom and the discussion of the structures and spectral behaviors of the ternary systems.

Experimental

Materials. L-Arginine, L-lysine dihydrochloride, L-ornithine monohydrochloride, L-glutamic acid (L-glu), L-aspartic acid (L-asp), L-alanine (L-ala), L-valine (L-val), iminodiacetic acid, 2,2'-bipyridine, 2-pyridinecarboxylic acid, and 2,6-pyridinedicarboxylic acid were purchased from Nakarai Chemicals, Ltd. All the chemicals used were of reagent grade or of highest grade available.

Synthesis of Mixed Ligand Copper(II) Complexes. [*Cu(ida)(L-lys)*]·*1/4H₂O.* Iminodiacetic acid (0.67 g, 5 mmol), L-lysine dihydrochloride (1.10 g, 5 mmol), and copper(II) perchlorate hexahydrate (1.85 g, 5 mmol) were dissolved in 30 ml of water, and the pH of the solution was adjusted at 7 with aqueous sodium hydroxide. After stirring for 1 h at room temperature the solution was concentrated *in vacuo* and filtered. Methanol was added to the filtrate to give blue crystals, which were recrystallized from aqueous methanol. Found: C, 34.88; H, 5.62; N, 12.25%. Calcd for $C_{10}H_{19}N_3O_6Cu \cdot 1/4H_2O$: C, 34.77; H, 5.69; N, 12.17%.

The following complexes were prepared at pH 7—10 in similar manners.

[Cu(ida)(L-arg)]·2H₂O. Found: C, 29.38; H, 5.58; N, 17.39%. Calcd for $C_{10}H_{19}N_5O_6Cu\cdot 2H_2O$: C, 29.66; H, 5.70; N, 17.30%.

[Cu(ida)(L-orn)]·2H₂O. Found: C, 29.88; H, 5.41; N, 11.41%. Calcd for $C_9H_{17}N_3O_6Cu\cdot 2H_2O$: C, 29.79; H, 5.84; N, 11.58%.

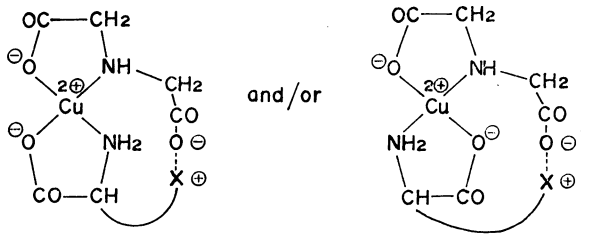
[Cu(pdca)(L-arg)]·H₂O. Found: C, 37.29; H, 4.70; N, 16.34%. Calcd for $C_{13}H_{17}N_5O_6Cu\cdot H_2O$: C, 37.10; H, 4.55; N, 16.64%.

[Cu(pdca)(L-orn)]·2.5H₂O. Found: C, 35.19; H, 5.15; N, 10.22%. Calcd for $C_{12}H_{15}N_3O_6Cu\cdot 2.5H_2O$: C, 35.51; H, 4.97; N, 10.35%.

Measurements of Absorption and CD Spectra. The spectroscopic measurements were performed in water or in aqueous ethanol at room temperature for the systems with the copper(II) : A : B ratios of 1 : 1 : 1 (ternary systems) and 1 : 2 : 0 and 1 : 0 : 2 (binary systems) at pH 5—11 at a copper(II) concentration of 5×10^{-3} M. The spectral samples were prepared from 0.1 M stock solutions of the ligands and copper(II) perchlorate. Because of the low solubility of 2,2′-bipyridine in water, a Cu(II)-bpy solution was used for preparation of the bpy-containing samples. The pH values were roughly adjusted with aqueous sodium hydroxide and dilute perchloric acid and finally determined after the spectroscopic measurements. The spectra of the Cu(L-glu)(L-arg) system were measured at different ionic strengths (μ) adjusted with sodium perchlorate. For the rest of the systems the ionic strengths of the solutions were not adjusted (μ= variable). Absorption spectra were recorded in the range 400—800 nm on a Union Giken SM-401 High Sensitivity recording spectrophotometer. CD spectra were measured in a 1- or 2-cm path length quartz cell in the range 350—800 nm with a JASCO MOE-1 spectropolarimeter.

Results and Discussion

Preparation of Mixed Ligand Copper(II) Complexes. Since iminodiacetate has a flexible molecular structure, it can be coordinated to copper(II) as a bidentate ligand, forming through the remaining carboxylate group electrostatic bondings with the positive group of the basic amino acid coordinated to the same copper(II) ion (**1**). Thus, iminodiacetate and the amino



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acids afforded the complexes [Cu(ida)(L-arg)], [Cu(ida)(L-orn)], and [Cu(ida)(L-lys)]. Although isolation of a ternary complex depends both on the stability and the solubility, it gives evidence of occurrence of a considerable amount of the ternary complex.

On the other hand, the inflexibility of the structure of pdca seems to affect the ternary complex formation, because attempts to prepare [Cu(pdca)(L-lys)] resulted in isolation of $Na_2[Cu(pdca)_2]$ under the conditions employed. Molecular models suggest that the interactions as illustrated in Scheme 1 are sterically unlikely to occur, so that the successful preparation of [Cu(pdca)(L-arg)] and [Cu(pdca)(L-orn)] might be ascribed to the statistical effect[9] and the complex-stabilizing effect of the pyridine ring as a π-acceptor.[7,10] The absorption spectral data of the ternary systems in the visible region (Table 1) apparently indicate the presence of rather large amounts of the binary species $Cu(pdca)_2$ and $Cu(B)_2$ in consequence of the lower stabilities of the ternary complexes.

Effects of Ionic Strength and Polarity of Solvent on the CD Magnitude. For the ternary systems with possible ligand-ligand interactions, the CD magnitudes expressed in terms of the relative magnitude, which assumes as unity the sum of the half magnitude ($1/2\Delta\varepsilon$) exhibited by each of the optically active ligands in the complex, have been found to be larger than unity.[5,6] In accordance with the observation about the Cu(edma)(B) systems,[5] where edma refers to ethylenediamine-*N*-monoacetate, the enhanced magnitude for the Cu(L-glu)(L-arg) system[6] has now been shown to be affected by the ionic strength of the solution and the polarity of the solvent used. The relative magnitude thus decreased from 1.3 (μ=variable) to 1.1 (μ=0.1) and 1.05 (μ=0.5) (Table 2). It might be suspected that the magnitude decrease at higher ionic strengths would result from the enhanced magnitudes for the binary systems to be compared. However, the molar extinction coefficients (ε) for the binary and ternary systems remain constant at different μ values (Table 2), indicating that the observed decrease is not due to the shifts of the equilibria. We may therefore infer that the decrease is caused by the weakened ligand-ligand interactions at higher salt concentrations. The magnitude increase in 10, 20, and 50% aqueous ethanol confirms that the interactions are electrostatic attractions which are favored in non-aqueous solvent.

L-orn-Containing Ternary Systems. The δ-amino group of ornithine is known to form an apical bonding with copper(II).[5,11,12] We observed in the previous study[6] that the systems Cu(L-asp)(L-orn) and Cu(L-glu)(L-orn) suffered complex CD spectral changes at pH>8. Figure 1 illustrates the pH dependence of their spectra, whose numerical data are summarized in Table 3. Since aspartate binds with copper(II) as a terdentate ligand with the β-carboxylate group at the apical position,[13] the spectral behaviors suggest that L-asp and possibly L-glu compete with the δ-amino group of L-orn for the apical coordination.

ida-Containing Ternary Systems. Table 4 shows that the absorption maxima of the Cu(ida)(B) systems ($\approx$665 nm) are between those of $Cu(B)_2$ ($\approx$620 nm) and $Cu(ida)_2$ (682 nm) and expectedly at longer wavelengths than those observed for the systems Cu(edma)(B) ($\approx$620 nm).[5]

The relative CD magnitudes for the Cu(ida)(B) systems in aqueous solution are 1.2—2.0 and are enhanced up to >1.7 in 50% aqueous ethanol (Table 4). These values are comparable with those of the systems containing two L-amino acids with charged side chains[6] but somewhat lower than those exhibited by the Cu(edma)(B) systems.[5] Both edma and ida may affect the CD spectra through molecular asymmetry originat-

TABLE 1. ABSORPTION SPECTRAL DATA FOR THE PYRIDINE-CONTAINING TERNARY SYSTEMS Cu(A)(B) (μ=variable)

Ligand B	Ligand A: pca			bpy			pdca		
	pH	ε	λ_{max}(nm)	pH	ε	λ_{max}(nm)	pH	ε	λ_{max}(nm)[a]
L-arg	9.9	48	636	10.0	59	611	9.9	38	739
	10.2[a]	60	638				10.5[a]	39	748
L-lys	9.8	49	632	9.2	58	608	10.0	38	710
	9.8[a]	61	636				10.0[a]	37	713
L-orn	not measured			7.5	58	607	7.9	37	737
				10.1	61	619	8.0[a]	38	746
							10.0	40	734
							10.2[a]	43	730
L-ala	8.9	49	633		59[b]	604[b]	9.9	37	740
	8.0[a]	59	636				10.7[a]	37	750
L-val	9.9	50	631		60[b]	604[b]	9.8	38	741
	10.1[a]	58	635				10.2[a]	38	750
L-glu	9.9	50	632	9.8	60	596	not measured		
	10.6[a]	59	638						
L-asp	not measured			8.7	53	614	not measured		

a) Measured in 50% aqueous ethanol. The pH values are pH meter readings. b) Taken from Ref. 7. c) The peaks were usually broad with a shoulder at 620—630 nm, which is indicative of the binary species Cu(L-amino acid)$_2$.

TABLE 2. EFFECTS OF IONIC STRENGTH AND POLARITY OF SOLVENT ON THE ABSORPTION (AB) AND CD SPECTRA FOR THE Cu(L-glu)(L-arg) SYSTEM

Medium[a]	Cu(L-glu)$_2$ pH	CD $\Delta\varepsilon$	CD λ_{max} (nm)	AB ε	AB λ_{max} (nm)	Cu(L-arg)$_2$ pH	CD $\Delta\varepsilon$	CD λ_{max} (nm)	AB ε	AB λ_{max} (nm)	Cu(L-glu)(L-arg) pH	CD $\Delta\varepsilon$	CD λ_{max} (nm)	AB ε	AB λ_{max} (nm)	Relative CD magnitude[b]
water (μ=var.)	8.5	-0.12_2	613	56	622	8.5	-0.11_1	598	56	622	8.5	-0.14_7	598	56	622	1.2_6
10% aq. ethanol	8.3	-0.12_3	612	59	619	7.9	-0.10_0	580	57	622	8.1	-0.15_6	601	59	621	1.3_4
20% aq. ethanol	8.2	-0.12_6	614	61	620	8.0	-0.10_1	580	58	620	8.5	-0.15_7	602	61	620	1.3_8
50% aq. ethanol	7.8	-0.13_8	616	62	620	8.1	-0.10_3	568	61	620	7.9	-0.17_3	600	63	620	1.4_4
water (μ=0.1)	7.7	-0.11_9	612	57	622	7.7	-0.12_0	592	55	622	7.6	-0.13_4	599	57	622	1.1_2
10% aq. ethanol (0.1 M $NaClO_4$)	8.7	-0.12_3	612	59	620	8.1	-0.12_0	586	56	622	8.3	-0.14_4	598	59	621	1.1_8
water (μ=0.5)	7.8	-0.13_2	615	57	622	7.7	-0.14_1	590	56	622	7.7	-0.14_3	607	57	622	1.0_5

a) Ionic strengths were adjusted with $NaClO_4$. The pH values in aqueous ethanol are pH meter readings.
b) Relative CD magnitude refers to $\Delta\varepsilon_{max}$(found)/$\Delta\varepsilon_{max}$(calcd).

ing from their fixation in a geometrical structure around copper(II) by the ligand-ligand bonding. The difference between edma and ida is that the imino nitrogen atom of the former can be asymmetric in the absence of the ligand-ligand interactions if it is coordinated to copper(II),[14-16] whereas the nitrogen atom of the latter cannot.

For the systems without the mentioned interactions, the CD magnitudes were found to be close to the estimated values and insensitive to addition of ethanol. The unexpectedly small magnitude for Cu(ida)(L-val) may partly be attributable to incomplete complex formation under the present conditions, in addition to the change in the spectral pattern in 50% aqueous ethanol.

These comparisons as well as those made earlier[5,6] indicate that the CD magnitudes are considerably enhanced when the ligand-ligand interactions occur and otherwise are reasonably additive even in some different ligand fields.[5,12]

Ternary Systems Involving a Pyridine Ring. (1) bpy-Containing Systems. The ternary systems Cu(bpy)(L-arg), Cu(bpy)(L-lys), and Cu(bpy)(L-glu) exhibited positive CD extrema around 560 nm, contrary to the negative peaks observed for the binary systems Cu(L-amino acid)$_2$ (Table 5). As Martin and Prados[7] reported for Cu(bpy)(L-phenylalanine), these anomalous spectral behaviors are probably caused by the electronic effects due to π-back donation, which has been pointed out in many ternary systems involving pyridine rings.[10]

Figure 2 shows that the CD spectral pattern of the

Table 3. Absorption and CD spectral data for the systems Cu(L-glu)(L-orn) and Cu(L-asp)(L-orn) at various pH values (μ=variable)

System	pH	CD Found $\Delta\varepsilon$	CD Found λ_{max}(nm)	CD Estimated[a] $\Delta\varepsilon$	CD Estimated[a] λ_{max}(nm)	Absorption ε	Absorption λ_{max} (nm)
Cu(L-glu)(L-orn)	7.5	-0.12_6	598	-0.09_0	604	55	625
	8.3	-0.10_0	590	-0.08_4	600	56	622
	8.8	-0.07_2	560	-0.04_6	554	58	624
	9.2	-0.04_5	538	-0.03_2	542	58	624
		$+0.03_6$	670	$+0.03_6$	≈740		
	9.5	$+0.15_7$	623	$+0.07_5$	631	57	627
	10.2	$+0.20_6$	623	$+0.15_6$	633	60	633
Cu(L-asp)(L-orn)	7.1	-0.07_1	630	-0.04_8	630	51	628
	9.4	$+0.03_6$	624	$+0.05_2$	630	54	631
	10.8	$+0.20_1$	618	$+0.21_0$	620	57	636

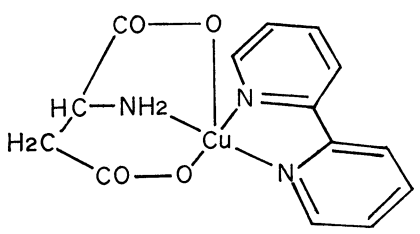
a) Estimated from the data for the corresponding binary systems (Refs. 5 and 6).

Table 4. Absorption and CD spectral data for the systems Cu(ida)(L-amino acid) (μ=variable)

L-Amino acid	pH	CD Found $\Delta\varepsilon$	CD Found λ_{max}(nm)	CD Estimated[a] $\Delta\varepsilon$	CD Estimated[a] λ_{max}(nm)	Absorption[c] ε	Absorption[c] λ_{max} (nm)	Relative CD magnitude[b]	Medium
L-arg	8.1	-0.07_8	632	-0.05_9	590	45	665	1.3	water
	10.9	-0.11_3	646	-0.05_3	575	49	676	2.1	50% aqueous ethanol
L-lys	9.2	-0.07_6	625	-0.06_4	604	45	664	1.2	water
	8.8	-0.10_5	643	-0.06_1	580	48	699	1.7	50% aqueous ethanol
L-orn	8.3	-0.06_6	638	-0.03_3	558	46	664	2.0	water
	9.1	-0.04_0	645	$+0.07_2$	635	46	664		water
	10.5	$+0.07_0$	620	$+0.23_1$	631	49	663		water
L-ala	8.2	-0.04_1	633	-0.04_0	633	46	666	1.0	water
	11.2	-0.04_0	640	-0.02_9	600	47	670	(1.4)[d]	50% aqueous ethanol
L-val	9.0	-0.09_0	638	-0.13_9	590	42	656	0.7	water
	9.1	-0.03_9	627	-0.12_4	580	50	622	(0.3)[d]	50% aqueous ethanol

a) Estimated from the data for the systems Cu(L-amino acid)$_2$ (Ref. 5). b) Relative CD magnitude refers to $\Delta\varepsilon_{max}$(found)/$\Delta\varepsilon_{max}$(calcd). c) The data for the Cu(ida)$_2$ system are as follows: λ_{max}=682 nm; ε=38(at pH 8.1 and 9.3). d) The anomalous value is probably due to the increase of the positive extremum at >700 nm.

Cu(bpy)(L-asp) system at pH 9.6 appears to be similar to that of the Cu(bpy)(L-orn) system at pH 10.1 with the sign inverted. The fact may be explained as arising from the octahedral distortion, which allows L-asp to coordinate as a terdentate ligand through its α-amino and β-carboxylate groups occupying the planar position as expressed by **2**, where the α-carboxylate group of L-asp appears as if it assumed the same arrangement as that of D-ornithine. This explanation is in line with the argument that has been made by Wilson *et al.*[12] for the CD spectra of the Cu(L-orn)$_2$ system in alkaline solution. Based on the calculations by the crystal field approximation, Gil *et al.*[17] recently suggested the distorted octahedral coordination around copper(II) for Cu(bpy)(L-amino acid) and Cu(phenanthroline)(L-amino acid). They indicated the possibility that the two chelate rings formed by the ligands might be perpendicular to each other.



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(2) pca- and pdca-Containing Systems. The pca-containing systems exhibited the absorption maxima centered around 635 nm (Table 1), from which formation of the ternary complexes may be inferred. For every L-amino acid employed, presence of pca in

TABLE 5. CD SPECTRAL DATA FOR THE PYRIDINE-CONTAINING SYSTEMS Cu(A)(B) (μ=variable)

Ligand	Ligand A								
	pca			bpy			pdca		
	pH	$\Delta\varepsilon$	λ_{max}(nm)	pH	$\Delta\varepsilon$	λ_{max}(nm)	pH	$\Delta\varepsilon$	λ_{max}(nm)
L-arg	9.9	-0.04_5	614	10.0	$+0.01_0$	560	9.9	-0.04_9	610
	10.2[a]	-0.04_5	590		$+0.00_7$	685	10.5[a]	-0.04_2	605
L-lys	9.8	-0.05_2	610	9.2	$+0.02_0$	578	10.0	-0.05_5	615
	9.8[a]	-0.05_5	600		$+0.01_3$	660	10.0[a]	-0.06_1	610
L-orn	not measured			7.5	$+0.05_6$	588	7.9	-0.01_8	580
				10.1	$+0.04_7$	603	10.0	$+0.09_7$	624
					-0.02_1	640	8.0[a]	-0.02_7	585
							10.2[a]	$+0.11_2$	622
L-ala	8.9	-0.02_9	626		$+0.02_4$[b]	570[b]	9.9	-0.03_3	630
	8.0[a]	-0.03_4	610		$+0.01_2$[b]	660[b]	10.7[a]	-0.03_2	625
L-val	9.9	-0.12_1	604		-0.06[b]	588[b]	9.8	-0.13_3	595
	10.9[a]	-0.12_7	584				10.2[a]	-0.10_9	585
L-glu	9.9	-0.05_0	620	9.8	$+0.02_4$	560	not measured		
	10.6[a]	-0.06_7	615		$+0.00_8$	680			
L-asp	not measured			8.7	$+0.01_0$	530	not measured		
					-0.05_4	628			

a) Measured in 50% aqueous ethanol. b) Taken from Ref. 7.

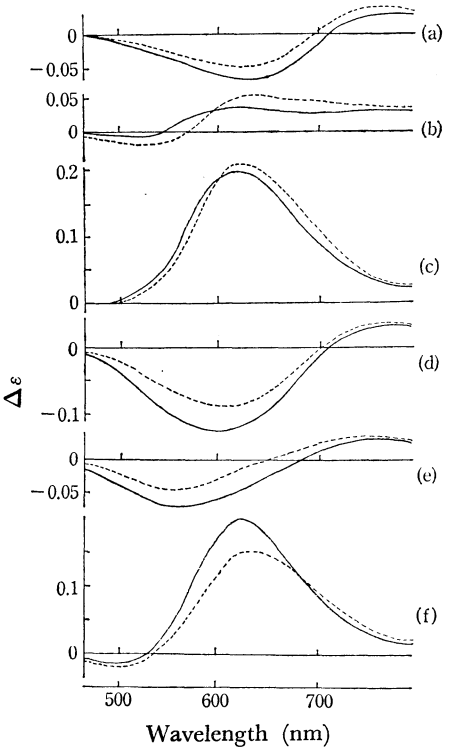

Fig. 1. Circular dichroism spectra of the systems Cu(L-asp)(L-orn) and Cu(L-glu)(L-orn).
Experimental curves: ——; Estimated curves: ----.
The estimated curves were obtained by plotting against wavelength the sums of the half magnitudes ($1/2\Delta\varepsilon$) exhibited by Cu(L-orn)$_2$ and Cu(L-asp)$_2$ or Cu(L-glu)$_2$ (Ref. 6).
(a) Cu(L-asp)(L-orn) pH 7.1; (b) Cu(L-asp)(L-orn) pH 9.4; (c) Cu(L-asp)(L-orn) pH 10.8; (d) Cu(L-glu)(L-orn) pH 7.5; (e) Cu(L-glu)(L-orn) pH 8.8; (f) Cu(L-glu)(L-orn) pH 10.2.

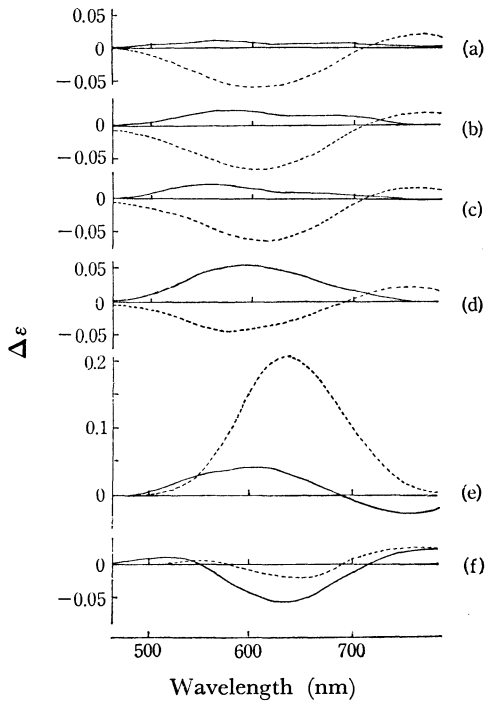

Fig. 2. Circular dichroism spectra of the systems Cu(bpy)(L-amino acid).
Experimental curves: ——; Estimated curves: ----.
The estimated curves were obtained by plotting against wavelength the half magnitudes ($1/2\Delta\varepsilon$) exhibited by Cu(L-amino acid)$_2$.
(a) Cu(bpy)(L-arg) pH 10.0; (b) Cu(bpy)(L-lys) pH 9.2; (c) Cu(bpy)(L-glu) pH 9.8; (d) Cu(bpy)(L-orn) pH 7.5; (e) Cu(bpy)(L-orn) pH 10.1; (f) Cu(bpy)(L-asp) pH 8.7.

the ternary system decreased the CD magnitude, but the effects were not so remarkable as to invert the CD sign.

The absorption spectra of the pdca-containing systems showed a broad peak with a shoulder, and the wavelengths of their CD peaks (Table 5) were very close to those of Cu(L-amino acid)$_2$.[5] These spectra are compatible with the view that the binary species contribute much to the observed spectral patterns. Considering that it is difficult to construct a molecular model having ligand-ligand interactions depicted in Scheme 1, pdca does not seem to provide a favorable condition for the intramolecular bonding, and the stabilities of the ternary complexes may be lower than those containing edma or ida in place of pdca.

Small CD magnitudes of the pdca series may indicate that L-amino acids are coordinated to copper(II) through the amino group in the tetragonal plane, whereas pdca occupies the rest of the coordination sites.[18] Murakami *et al.*[19] reported that L-amino acids in the mixed ligand complexes, Cu(diethylenetriamine)(L-amino acid), are bonded to copper(II) in neutral solution through the amino group in the square plane and the carboxylate group interacting at the apical position, which is occupied by a hydroxyl ion in alkaline solution.

The present observations demonstrate that the pyridine ring in the ternary systems studied does change the CD patterns probably through the π-back donation associated with the copper(II)-pyridine bonding and thus may affect the formation of mixed ligand complexes.

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