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Metal Complexes with Amino Acid Amides. II. Preparations and Circular Dichroism Behavior of the Copper(II) Complexes

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Planar bis-type complexes of copper(II) with L-leucine-, L-valine-, L-phenylalanine- and L-proline-amidate ligands have been newly synthesized and characterized mainly spectroscopically together with the known complexes with glycine- and L-alanine-amidates. The geometrical structures of these [Cu(N)$_4$]-type complexes have been tentatively determined. The blue colored complexes, Cu(glycine-amide)$_2$SO$_4$ and its L-alanine amide analogue, have been isolated, too. The circular dichroism spectra of the complexes containing optically active ligands have been measured in various solvents and discussed in comparison with the available data for square planar d^8-complexes or for amino acidato complexes. A number of interesting relations were observed among the circular dichroism spectra of the copper(II) and the square planar d^8 complexes with optically active bidentate ligands.

It has been well known that most of copper(II) complexes have tetragonally distorted octahedral structures.[1] Since the degree of the distortion, which has been called tetragonality, seems to vary continuously up to the limit of a square planar structure,[2] there are some difficulties in studying the structures of copper(II) complexes in solution. Jørgensen has marked out the tetragonalities of various copper(II) complexes in solution by comparing their electronic spectra with those of the corresponding nickel(II) complexes which have essentially octahedral symmetry.[2] This method, however, cannot be applied to a group of the copper(II) complexes, to which diamagnetic square planar, not octahedral, nickel(II) complexes correspond.

Yasui *et al.*[3] have ascertained experimentally the possibility to resolve the ligand field bands of copper(II) complexes in solution into their split components by means of the circular dichroism (CD), and Wellman *et al.*[4] have suggested a relationship between the signs (and the magnitudes also) of the Cotton effects and the chelate ring conformations of the amino acidato copper(II) complexes. This suggestion has been somewhat modified by Martin *et al.*[5] In these circumstances, it is thought to be desirable to apply a CD study to the copper(II) complexes to which diamagnetic planar nickel(II) complexes correspond.

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[1] L. E. Orgel and J. D. Dunitz, *Nature,* **179**, 462 (1957).

[2] C. K. Jϕrgensen, *Acta Chem. Scand.,* **9**, 1362 (1955).

[3] T. Yasui, J. Hidaka and Y. Shimura, *J. Am. Chem. Soc.,* **87**, 2762 (1965); T. Yasui, This Bulletin, **38,** 1746 (1965).

[4] K. M. Wellman, T. G. Mecca, W. Mungall and C. R. Hare, *J. Am. Chem. Soc.,* **89**, 3646, 3647 (1967); **90**, 805 (1968); *Chem. Eng. News,* **48**, (Oct. 2, 1967).

[5] R. B. Martin, J. M. Tsangaris and J. W. Chang, *J. Am. Chem. Soc.,* **90**, 821 (1968).

In the first paper of this series,[6] the two types of nickel(II) complexes, Ni(α-amino-acid-amide)$_2$$SO_4\cdot xH_2O$ and Ni(α-amino-acid-amidate)$_2$$\cdot xH_2O$, have been reported. The copper(II) complexes (R-type)[7] corresponding to the latter type of nickel(II) complexes with glycine-, L-alanine- or D,L-leucine-amidate have been already prepared,[8] but none of them has been studied concerning their electronic spectra.

In the present paper, we report the preparations of some new complexes of R-type with L-leucine-, L-valine-, L-phenylalanine- or L-proline-amidate and of another new type (B-type)[7] of the copper(II) complexes, Cu(glyaH)$_2$$SO_4$ and Cu(L-alaaH)$_2$$SO_4\cdot H_2O$,[9] which corresponds to the former type of nickel(II) complexes cited above. The electronic absorption and CD spectral data of all these complexes obtained are discussed in relation to their structures.

Experimental

Preparation. *1) Amino Acid Amides.*[9] The following six amino acid amides used as ligands were derived from the corresponding amino acids by the similar method as described in literature.[10]

glyaH (from chloroform); mp 67.5—68.5°C.

L-alaaH (from chloroform); mp 83—84°C; $[\alpha]_{589}=+11.1°$.

L-leuaH (from benzene); mp 103—104°C; $[\alpha]_{589}=+7.3°$.

Found: N, 21.60%. Calcd for $C_6H_{14}N_2O$: N, 21.52%.

L-valaH (from benzene); mp 87—89°C; $[\alpha]_{589}=+12.2°$.

Found: N, 24.27%. Calcd for $C_5H_{12}N_2O$: N, 24.33%.

L-phalaaH (from benzene); mp 95—96°C; $[\alpha]_{589}=+17.8°$.

Found: N, 17.14%. Calcd for $C_9H_{12}N_2O$: N, 17.06%.

L-proaH (from benzene); mp 106.5—107.5°C; $[\alpha]_{589}=-79.3°$.

Found: N, 24.56%. Calcd for $C_5H_{10}N_2O$: N, 24.54%.

The measurements of the specific rotations were made for the aqueous solutions ($c=10$) at room temperature (19—21°C). All the melting points were uncorrected.

2) Bis(amino-acid-amidato)copper(II) Complexes. The general preparation procedure of these complexes are as follows. Eleven milliformoles (mF) of amino acid amide was dissolved in 5—30 m*l* of water and the solution was added to the solution containing 1.0 g (5 mF) of copper(II) acetate monohydrate in 15 m*l* of water. Then 5—10 m*l* of the aqueous solution containing 0.40 g (10 mF) of sodium hydroxide was added dropwise to the bluish violet solution with mechanical stirring. The desired complex was crystallized out from the resulted reddish violet solution[11] (filtered if necessary) by an appropriate procedure of the followings, namely, vacuum concentration below 35°C, addition of ethanol (or methanol) and then of ether, or the combined procedure.

Freshly prepared copper(II) hydroxide was also good starting material, which could be used in place of copper(II) acetate monohydrate and sodium hydroxide in the above procedure. All the complexes in this category were obtained in good yields, and only one kind of crystals[12] could be isolated for each of the ligands. Recrystallization was made by one of the following procedures: (I) ethanol and then ether were added to the concentrated aqueous solution, (II) ether was added to the concentrated methanolic solution, (III) the aqueous solution was concentrated *in vacuo*, or (IV) the methanolic solution was concentrated by evaporating in air.

Bis(glycine-amidato)copper(II) Monohydrate: Cu(glya)$_2$$\cdot H_2O$. Recrystallized by I.

Found: C, 21.31; H, 5.44; N, 24.65%. Calcd for $C_4H_{12}N_4O_3Cu$: C, 21.08; H, 5.31; N, 24.61%.

Bis(L-alanine-amidato)copper(II): Cu(L-alaa)$_2$. Recrystallized by I.

Found: C, 30.22; H, 5.37; N, 23.63%. Calcd for $C_6H_{14}N_4O_2Cu$: C, 30.31; H, 5.94; N, 23.57%.

Bis(L-leucine-amidato)copper(II): Cu(L-leua)$_2$. Recrystallized by IV and dried over calcium chloride; pink needles; soluble in methanol and moderately soluble in water and ethanol. The raw product was the mixture of the two forms of crystals, the needle and the plate: infrared spectra in NaCl region, however, showed no difference between them.

Found: C, 44.40; H, 8.07; N, 17.19%. Calcd for $C_{12}H_{26}N_4O_2Cu$: C, 44.78; H, 8.14; N, 17.40%.

Bis(L-valine-amidato)copper(II) Dihydrate: Cu(L-vala)$_2$$\cdot 2H_2O$. Recrystallized by (IV) and dried in air; violet plates; soluble in water, methanol and ethanol to give reddish violet solutions.

Found: C, 36.48; H, 7.58; N, 16.79%. Calcd for $C_{10}H_{26}N_4O_4Cu$: C, 36.41; H, 7.94; N, 16.98%.

Bis(L-phenylalanine-amidato)copper(II) Dihydrate and Anhydrate: Cu(L-phalaa)$_2$$\cdot 2H_2O$ and Cu(L-phalaa)$_2$.

Dihydrate: recrystallized by (III) and dried in air; reddish violet plates; soluble in water, methanol and ethanol.

Found: C, 50.69; H, 6.12; N, 13.13%. Calcd for $C_{18}H_{26}N_4O_4Cu$: C, 50.75; H, 6.15; N, 13.15%.

Anhydrate: derived from the dihydrate by drying *in vacuo* over phosphorus pentoxide overnight; pink solid.

Found: C, 55.15; H, 5.74; N, 14.26%. Calcd for

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[6] T. Komorita, J. Hidaka and Y. Shimura, This Bulletin, **41**, 854 (1968).

[7] R-type: red colored Cu(II) complex, B-type: blue colored Cu(II) complex.

[8] P. Bergell and T. Brugsch, *Z. physiol. Chem.*, **67**, 97 (1910); M. M. Rising and P. S. Yang, *J. Biol. Chem.*, **99**, 755 (1933).

[9] The following abbreviations are used for ligands: glyaH=glycine amide, alaaH=alanine amide, leuaH=leucine amide, valaH=valine amide, phalaaH=phenylalanine amide, proaH=proline amide, glyH=glycine, alaH=alanine, leuH=leucine, valH=valine, proH=proline, hyproH=hydroxyproline, piaH=α-picoline amide, biuH$_2$=biuret and glyglyH$_2$=glycylglycine.

[10] P. S. Yang and M. M. Rising, *J. Am. Chem. Soc.*, **53**, 3183 (1931); G. Hillmann, *Z. Naturforsch.*, **1**, 682 (1946).

[11] When L-leuaH or L-phalaaH was used as the ligand, the desired crystals separated out at this stage.

[12] As for the L-leucine amidato complex, see below.

$C_{18}H_{22}N_4O_2Cu$: C, 55.44; H, 5.69; N, 14.37%.

Bis(L-proline-amidato)copper(II) Dihydrate: Cu(L-proa)$_2\cdot$2H_2O. Recrystallized by (II) and dried *in vacuo* over calcium chloride; pink needles; soluble in water, methanol, ethanol and *N,N*-dimethylformamide, and slightly soluble in pyridine.

Found: C, 36.85; H, 6.83; N, 17.10%. Calcd for $C_{10}H_{22}N_4O_4Cu$: C, 36.86; H, 6.81; N, 17.19%.

3) Bis(amino-acid-amide)copper(II) Sulfates. Bis(glycine-amide)copper(II) Sulfate: Cu(glyaH)$_2$SO$_4$. Copper(II) sulfate pentahydrate (0.84 g) and 0.50 g of glycine amide were dissolved in 5 m*l* of water. After stirring the solution for several min, the blue crystals were obtained by adding a small amount of methanol to the blue solution. This complex was recrystallized from the aqueous solution by adding a small amount of methanol, washed with methanol and then with ether, and dried *in vacuo* over phosphorus pentoxide overnight; very soluble in water but insoluble in methanol and ethanol.

Found: C, 15.34; H, 4.00; N, 17.51%. Calcd for $C_4H_{12}N_4O_6SCu$: C, 15.61; H, 3.93; N, 18.21%.

Bis(L-alanine-amide)copper(II) Sulfate Monohydrate: Cu(L-alaaH)$_2$SO$_4\cdot H_2O$. Preparation and purification of this complex was carried out in the same way as given for the corresponding complex with glycine amide. The yield was almost quantitative. Shiny blue plates; very soluble in water but insoluble in methanol and ethanol.

Found: C, 20.70; H, 4.77; N, 15.11; H_2O, 4.94%. Calcd for $C_6H_{18}N_4O_7SCu$: C, 20.37; H, 5.13; N, 15.83; H_2O, 5.09%.

The water of crystallization was analyzed by the weight loss under aspirator pressure at 60°C.

4) Glycinato(glycine-amidato)copper(II) Monohydrate: Cu(gly)(glya)$\cdot H_2O$. Bis(glycine-amidato)copper(II) in aqueous solution undergoes stepwise hydrolysis of the ligands during several weeks at room temperature and finally changes into bis(glycinato)copper(II). Glycinato(glycine-amidato)copper(II) monohydrate, an intermediate of the hydrolysis, separated out when a concentrated aqueous solution of Cu(glya)$_2\cdot H_2O$ was allowed to stand on a warm water bath for several hours. This intermediate complex was also obtained easily by concentrating rapidly the aqueous solution containing Cu(gly)$_2\cdot H_2O$ and Cu(glya)$_2\cdot H_2O$ (1 : 1). Recrystallization was made by adding methanol to the aqueous solution of the complex. Shiny violet plates; soluble in water, slightly soluble in methanol and insoluble in ethanol.

Found: C, 21.16; H, 4.90; N, 18.34%. Calcd for $C_4H_{11}N_3O_4Cu$: C, 21.01; H, 4.85; N, 18.37%.

5) *Bis(amino-acid-amide)copper(II) Sulfate Solutions.* The five and ten milliformoles per liter aqueous solutions of bis(amino-acid-amide)copper(II) sulfate were prepared for the absorption and CD spectral measurements, respectively: one (or two) milliliter(s) of the 100 mF $CuSO_4$ and 0.2 mF (or 0.4 mF) of the ligand (L-leuaH, L-valaH, L-phalaaH or L-proaH) were dissolved in water, and the total volume was adjusted to 20 m*l*. Copper (II) sulfate pentahydrate used was a Special Grade reagent produced by Wako Pure Chemical Industries, Ltd.

Measurements. The absorption, diffuse reflectance and CD measurements were made by a Beckman DU spectrophotometer, a Hitachi EPU-2A spectrophotometer and a Roussel-Jouan dichrographe, respectively, at room temperature. Ethanol and methanol used for these measurements as the solvents were dehydrated by refluxing with corresponding magnesium alkoxide and distilled. The solvent *N,N*-dimethylformamide was a commercial Spectro Grade one produced by Dojindo & Co., Ltd. No significant change of the spectra was found during every measurement.

Results and Discussion

1) N–O and N–N Coordination of the α-

TABLE 1. ABSORPTION AND REFLECTANCE SPECTRAL DATA OF THE B-TYPE COMPLEXES

Complex[a]	Solvent or condition[b]	Maximum[c] ν_{max} (log ε)	Band-width[c,d] δ	Concentration[e]
Cu(glyaH)$_2$SO$_4$	(S)	14.9	4.9	—
	(W)	15.2 (1.53)	5.7	6.5
Cu(L-alaaH)$_2$SO$_4\cdot H_2O$	(S)	15.3	4.9	—
	(W)	15.6 (1.49)	5.8	5.5
Cu(L-leuaH)$_2$SO$_4$	(W)[f]	15.7 (1.59)	6.0	5.0
Cu(L-valaH)$_2$SO$_4$	(W)[f]	15.7 (1.57)	6.4	5.0
Cu(L-phalaaH)$_2$SO$_4$	(W)[f]	15.6 (1.56)	6.1	5.0
Cu(L-proaH)$_2$SO$_4$	(W)[f]	16.0 (1.65)	6.0	5.0
trans-Cu(gly)$_2\cdot H_2O$	(S)[g]	16.3	4.8	—
cis-Cu(gly)$_2\cdot H_2O$	(S)[g]	15.7	4.0	—
	(W)[g]	15.9 (1.65)	4.7	5.0
[Cu(piaH)$_2$(OH$_2$)$_2$]Cl$_2$	(W)[h]	14.5 (1.47)	5.0	7.15

a) Abbreviations: footnote 9.
b) Abbreviations: S=solid, W=water.
c) Wave number's are given in 10^3 cm^{-1} unit.
d) Apparent band-width at half extinction.
e) 10^{-3} F unit.
f) These solutions were prepared as described in the Experimental section 5).
g) Ref. 13; either the trans or the cis complex gives the same spectrum in aqueous solution.
h) Ref. 14 and M. Sekizaki, private communication.

Amino Acid Amides. In Table 1, the electronic absorption data of the B-type complexes are summarized with some referable data. It has been concluded in the former paper[6] that α-amino acid amide chelates through an amide oxygen and an amino nitrogen to a central metal ion in the bis(amino-acid-amide)nickel(II) complexes. The N–O coordination is also inferred for the corresponding B-type copper(II) complexes, $Cu(glyaH)_2SO_4$ and $Cu(L\text{-}alaaH)_2SO_4\cdot H_2O$, in the solutions and in the solid states from their electronic spectra. Another support for the common type of coordination between the bis(amino-acid-amide)-copper(II) and -nickel(II) complexes is furnished from the infrared (IR) spectra. The IR spectra of all these complexes show two very strong bands, which are very specific to this type of complexes, in each of their 6μ regions.[15] It may be possible to suggest that the $[Cu(L\text{-amino-acid-amide})_2(OH_2)_2]^{2+}$ ion is only the probable species in the solution.[16]

The electronic absorption and reflectance data of the R-type complexes are summarized with some references in Table 2. The $K_2[Cu(biu)_2]\cdot 4H_2O$[18] and $K_2Cu(glygly)_2\cdot 6H_2O$[20] have been known to have planar $Cu(N)_4$ structure. From the comparison with the electronic spectral data in the solutions and in the solid states and the referable data, it may be concluded that the amino acid amidato ligands in the R-type complexes have the N–N coordination through an amino nitrogen and an amidato nitrogen. The same conclusion has been previously applied for the corresponding nickel(II) and palladium(II) complexes.[6]

2) Solvation and Geometrical Isomerism.

The following factors may be inferred to influence considerably the ligand field bands of both the B- and R-type complexes: (a) interaction between copper(II) ion and solvent molecules along with the normal of the coordination square, (b) geometrical isomerism of the complexes, and (c) electronic and structural characteristics of the ligands.

With respect to the five R-type complexes with the L-amino acid amidato ligands, the absorption maxima (ν_{max}) are distributed within the ranges 19000—19500 in water and 19900—20100 cm^{-1} in ethanol respectively, as shown in Table 2. This fact reveals that the effect of the factor (c) is relatively small among the five L-amino acid amidates. The solvent dependence of ν_{max}, derived from the factor (a), is clearly larger than the effect (c). For instance, the difference of ν_{max}'s between the aqueous and the dimethylformamide solutions of $Cu(L\text{-}proa)_2$ is 1200 cm^{-1} and the one between the aqueous and the chloroform solutions of $Cu(pia)_2$, 1800 cm^{-1} (Table 2). The difference of ν_{max}'s between *trans*- and *cis*-$Cu(gly)_2\cdot H_2O$, derived from the factor (b), is only 600 cm^{-1} (Table 1). However, the factor (b) may probably be intensified in the R-type complexes because of the increased covalency in the coordination square.

Now, the ν_{max}'s of the ligand field bands of the R-type complexes shift to lower wave number's and the apparent band widths (δ) decrease in the following order of solvents (or condition): solid→ dimethylformamide → ethanol → methanol → water, except for $Cu(L\text{-}vala)_2\cdot 2H_2O$ and $Cu(L\text{-}phalaa)_2\cdot 2H_2O$ in the solid states (Table 2). This spectral behavior including the case of $Cu(L\text{-}phalaa)_2\cdot 2H_2O$ may be understood on the basis of the donor properties of the solvent molecules, that is, of the factor (a). The ν_{max} value of $Cu(L\text{-}vala)_2\cdot 2H_2O$ in only the solid state exceedingly deviates from the above sequence and, in fact, is lower by as much as 1000 cm^{-1} than the value in the aqueous solution (Table 2). This cannot be explained by the coordination of water, that is, factor (a), and the factor (b) should be taken into account. Judging from the facts that most of the copper(II) bis-chelated complexes, the structures of which have been known, have trans ones[16] and that the ν_{max} of *cis*-$Cu(gly)_2\cdot H_2O$ is lower than that of the corresponding trans complex (Table 1), the geometrical structure of $Cu(L\text{-}vala)_2\cdot 2H_2O$ may be tentatively assigned to cis in the solid state and, on the contrary, to trans in the aqueous and the alcoholic solutions. Another support to the trans structure in solution may be furnished by the following observation: when a methanolic solution containing the crystals was rapidly concentrated *in vacuo*, a small amount of red crystals, which may presumably be trans, was found mixed together with the ordinary violet crystals. The other five complexes of R-type may be tentatively considered to have trans structures

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13) T. Yasui and Y. Shimura, This Bulletin, **39**, 604 (1966) and T. Yasui, private communication.

14) M. Sekizaki and K. Yamasaki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 1053 (1966).

15) T. Komorita, J. Hidaka and Y. Shimura, unpublished.

16) H. C. Freeman, "The Biochemistry of Copper," ed. by Peisach, P. Aisen and W. E. Blumberg, Academic Press, New York, N. Y. (1966), p. 77; according to a number of the X-ray analytical data, it may be reasonable to consider relatively strongly bounded $Cu(N)_2(O)_2$ square planar moieties in these complexes. See also the Discussion section 2) of the present paper.

17) Y. Nakao, K. Sakurai and A. Nakahara, This Bulletin, **39**, 1608(1966) and Y. Nakao, private communication.

18) H. C. Freeman, J. E. W. L. Smith and J. C. Taylor, *Acta Cryst.*, **14**, 407 (1961).

19) M. Kato, Y. Komuro and K. Sone, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **78**, 896 (1957).

20) A. Sugihara, T. Ashida, Y. Sasada and M. Kakudo, *Acta Cryst.*, **B24**, 203 (1968); in this complex, two water molecules are linked to the copper(II) along with the normal of the $Cu(N)_4$ plane with the Cu–O distance, 2.77 Å.

TABLE 2. ABSORPTION AND REFLECTANCE SPECTRAL DATA OF THE R-TYPE COMPLEXES

Complex[a)]	Solvent or condition[b)]	Maxima[c,f)] ν_{max} (log ε)	Band-width[c,d)] δ	Concentration[e)]
$Cu(glya)_2 \cdot H_2O$	(S)	19.2	6.1	—
	(W)	18.7 (1.67)	5.6	7.1
	(Me)	18.9 (1.71), ~29 sh	5.8	4.0
$Cu(\text{L-alaa})_2$	(S)	20.7	6.2	—
	(W)	19.1 (1.74)	5.4	2.8
	(Me)	19.6 (1.77), ~29 sh	5.9	2.7
	(Et)	20.0 (1.78), ~29 sh	5.9	2.8
$Cu(\text{L-leua})_2$	(S)	21.2	6.4	—
	(W)	19.4 (1.76)	5.5	5.4
	(Me)	19.8 (1.79), ~29 sh	5.8	3.1
	(Et)	20.0 (1.82), ~28.5 sh	6.0	1.3
$Cu(\text{L-vala})_2 \cdot 2H_2O$	(S)	18.5	6.5	—
	(W)	19.5 (1.74)	5.5	5.0
	(Et)	20.1 (1.78), ~28 sh	5.8	5.0
$Cu(\text{L-phalaa})_2 \cdot 2H_2O$	(S)	19.6	6.4	—
$Cu(\text{L-phalaa})_2$	(S)	20.7	6.7	—
	(W)	19.2 (1.73)	5.4	5.0
	(Et)	19.9 (1.78), ~28.5 sh	5.6	5.0
$Cu(\text{L-proa})_2 \cdot 2H_2O$	(S)	~13 sh, 20.9	5.9	—
	(W)	19.5 (1.90)	5.5	5.0
	(Et)	20.1 (1.93)	5.8	5.0
	(DMF)	20.7 (1.96)	5.9	5.0
$[Cu(pia)_2] \cdot 5H_2O$	(W)[g)]	17.1 (1.68)	5.8	0.98
	$(CHCl_3)$[g)]	18.9 (1.86)	5.2	0.38
$K_2[Cu(glygly)_2] \cdot 6H_2O$	(W)[h)]	18.0 (1.72)	6.2	10
$K_2[Cu(biu)_2] \cdot 4H_2O$	(S)[i)]	19.8		—
$[Cu(biu)_2]^{2-}$	(W)[j)]	19.8 (1.65)		

a) Abbreviations: footnote 9.
b) Abbreviations: S=solid, W=water, Me=methanol, Et=ethanol and DMF=*N*,*N*-dimethylformamide.
c), d) and e) See Table 1.
f) shoulder.
g) See Table 1.
h) In aqueous solution (1 F $glyglyH_2$ and 2 F KOH); Ref. 17.
i) Ref. 18.
j) Ref. 19.

both in the solid states and in the solutions from the above discussion.

The ν_{max}'s of $Cu(glya)_2 \cdot H_2O$ both in the solid state and in the solutions considerably shift to lower wave number's than those in the corresponding conditions of the other R-type complexes, which are considered to be trans (Table 2). Similar shift is also observed for $Cu(glyaH)_2SO_4$ compared with the other B-type complexes (Table 1). These behavior should be attributed to the combined effect of the factors (a) and (c).

More quantitative informations about the factor (a) in these complexes may be supplied by comparing their ν_{max}'s with those of the corresponding nickel(II) complexes.[6,15] As far as the B-type is concerned, the tetragonality ratios can be obtained by Jørgensen's definition[2] as shown in Table 3; these values are very close to the value, 1.60, for bis(glycinato)copper(II). Now, concerning the R-type, the corresponding nickel(II) complexes are diamagnetic square planar ones. Neverthless we applied the ratio, ν_{Cu}/ν_{Ni}, also to these complexes, using the ligand field ν_{max}'s of the planar nickel(II) complexes (Table 3). Bis(biuretato)-cuprate(II) and -nickolate(II) may be regarded as "true" square planar complexes, since each the complex reveals the same ν_{max} value between in the aqueous solution and in the solid state. Therefore, the value, 0.91, may be considered to suggest that the nickel(II) complex has larger tetragonality than the copper(II) complex. (This value could be expected to be larger than 1 for a certain tetragonality, or for a certain octahedral field splitting (Δ), after taking the interelectronic repulsion of d^8-configuration into account.) This consideration is compatible with the theory that one electron

TABLE 3. ν_{Cu}/ν_{Ni} VALUES

B-type complex[a]	Solvent or condition	ν_{Cu}	ν_{Ni}[b]	ν_{Cu}/ν_{Ni}
(glyaH)$_2$(OH$_2$)$_2$	(W)	15.2	9.7[f]	1.57
(L-alaaH)$_2$(OH$_2$)$_2$	(W)	15.6	9.7[f]	1.61
(piaH)$_2$(OH$_2$)$_2$	(W)[c]	14.5	9.8	1.48
R-type complex				
(glya)$_2$	(S)[d]	19.2	22.9[f]	0.84
	(W)	18.7	23.1[g]	0.81
(L-alaa)$_2$	(S)	20.7	23.7[f]	0.87
	(W)	19.1	23.2[g]	0.82
	(Me)	19.6	23.4[f]	0.84
(L-leua)$_2$	(Me)	19.8	23.4[f]	0.85
(L-vala)$_2$	(Et)	20.1	23.3[g]	0.86
(L-phalaa)$_2$	(Et)	19.9	23.1[g]	0.86
(L-proa)$_2$	(W)	19.5	23.0[g]	0.85
	(Et)	20.1	23.1[g]	0.87
	(DMF)	20.7	23.4[g]	0.88
(pia)$_2$	(CHCl$_3$)[c]	18.9	23.1	0.82
(biu)$_2$	(S, W)[e]	19.8	21.7	0.91

a) Abbreviations: footnote 9.
b) Ref. 2 for B-type and see text for R-type.
c) Ref. 14.
d) Monohydrate.
e) Refs. 18 and 19.
f) Ref. 6.
g) Footnote 15.

TABLE 4. CD EXTREMA OF THE B- AND THE R-TYPE COMPLEXES

Complex[a]	Solvent	Extrema[b]	Concentration[c]
Cu(L-alaaH)$_2$SO$_4$·H$_2$O	(W)	15.7 (−0.12)	40
Cu(L-leuaH)$_2$SO$_4$	(W)[d]	16.5 (−0.14)	10
Cu(L-valaH)$_2$SO$_4$	(W)[d]	17.2 (−0.22)	10
Cu(L-phalaaH)$_2$SO$_4$	(W)[d]	16.5 (−0.28)	10
Cu(L-proaH)$_2$SO$_4$	(W)[d]	14.8 (+0.13), 18.7 (−0.07)	10
Cu(L-alaa)$_2$	(W)	18.5 (−0.34)	20
	(Et)	18.5 (−0.33), 22.8 (+0.02)	20
Cu(L-leua)$_2$	(W)	18.3 (−0.43)	5
	(Me)	18.5 (−0.38)	15
	(Et)	18.4 (−0.38)	1
Cu(L-vala)$_2$·2H$_2$O	(W)	13.9 (+0.005), 18.7 (−0.45)	20, 10[e]
	(Et)	13.6 (+0.004), 18.5 (−0.50), 22.8 (+0.03)	20, 10[e]
Cu(L-phalaa)$_2$	(W)	13.6 (+0.004), 17.9 (−0.28), ~20 sh (−)	20, 10[e]
	(Et)	17.3 (−0.31), ~20 sh (−)	20, 10[e]
Cu(L-proa)$_2$·2H$_2$O	(W)	13.9 (+0.007), 17.6 (−0.30), 21.3 (−0.42)	20, 10[e]
	(Et)	17.2 (−0.44), 21.9 (−0.52)	20, 10[e]
	(DMF)	16.7 (−0.25), 19.1 (+0.20), 22.1 (−0.58)	8.5, 5[e]

a) Abbreviations: footnote 9.
b) Wave number's are given in 10^3 cm^{-1} unit and the intensities, $\varepsilon_l-\varepsilon_d$ in parentheses; sh=shoulder.
c) 10^{-3} F unit.
d) See f) of Table 1.
e) The more concentrated solution of these two was used to detect weak extrema at lower wave number's.

and none, respectively, is accommodated in the σ-antibonding (x^2-y^2)-orbital in the ground state of the copper(II) and nickel(II) complexes. The R-type copper(II) complexes seem to be more extensively influenced by the factor (a) than the corresponding nickel(II) complexes. However, it may be reasonable to regard the R-type complexes, including even the glycine amidato one, as "square planar" complexes since their ν_{Cu}/ν_{Ni} values distribute continuously in a rather narrow range, 0.81—0.88, and the minimum is comparable with 0.82 for the bis(picoline-amidato) complexes in "chloroform." It may be worthwhile to note that the ν_{max}'s of the B-type complexes shift to higher wave number's and the δ's increase with changing the condition from the solid states to the aqueous solutions, in contrast with those of the R-type.

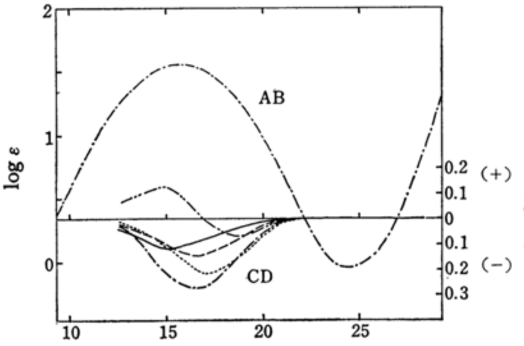

Fig. 1. Absorption and CD spectra of Cu(L-amino-acid-amide)$_2$SO$_4$ in water.
——— alaaH-; — — — leuaH-; ·········· valaH-; —·—·— phalaaH-; and —··—··— proaH-complexes.

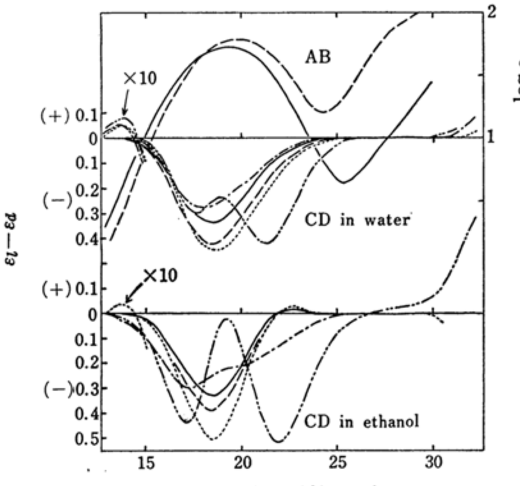

Fig. 2. Absorption and CD spectra of Cu(L-amino-acid-amidate)$_2$.
Absorption curves of Cu(L-phalaa)$_2$; —— in water; and — — — in ethanol.
CD crucves in water and in ethanol: —— alaa-; — — — leua-; ·········· vala-; —·—·— phalaa-; and —··—··— proa-complexes.

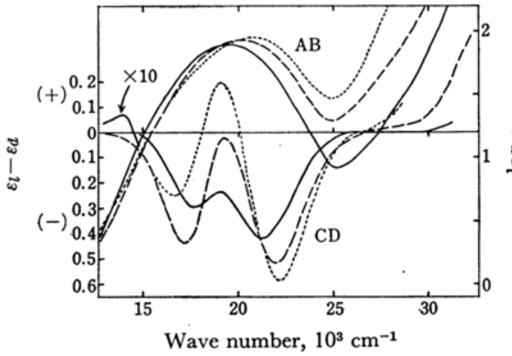

Fig. 3. Absorption and CD curves of Cu(L-proa)$_2$. ——— in water; — — — in ethanol; and ·········· in DMF.

3) CD of the Complexes. In general, the negative CD components are dominant in the ligand field band region of the B- and the R-type complexes with the L-optically active ligands (Table 4 and Figs. 1—3); the CD behavior of Cu(L-proaH)$_2$SO$_4$ in the aqueous solution is only the exception. It has been reported[3)] that bis(L-α-amino-acidato)copper(II) complexes also exhibit ligand field CD bands, the negative components of which are dominant, too, except for those of the L-prolinato and the L-hydroxyprolinato complexes. Wellman *et al.*[4)] have explained the negative Cotton effect in this region on the assumption of the puckered conformation of amino acidato chelate ring as of ethylenediamine one (Fig. 4c).

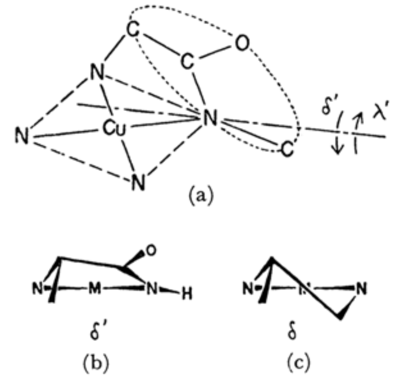

Fig. 4. Conformations of chelate rings of (a) glygly$^-$ in K$_2$Cu(glygly)$_2$·6H$_2$O (Arrows: the C–CO–N–C plane is inclined), (b) L-amino acid amidate and (c) (+)-propylenediamine.

Informations about the conformation of α-amino acidato or α-amino acid amidato ligand will be obtained from the X-ray analytical data for *cis*-

$Cu(gly)_2 \cdot H_2O$[21] or $K_2Cu(glygly)_2 \cdot 6H_2O$.[20] In the latter complex, both the $Cu(N)_4$ square and the C–CO–N–C moiety of the ligand have good planarity respectively, but these two planes are inclined to each other, intersecting along the axis which passes through the amidato nitrogen and nearly bisects the Cu–N(amino) bond as shown in Fig. 4a. The conformation of the glycinato chelate ring in *cis*-$Cu(gly)_2 \cdot H_2O$ seems to be very similar to that of the glycylglycinato chelate ring mentioned above, and is considerably different, especially around the coordinated oxygen, from that assumed by Wellman *et al.* as shown in Figs. 4b and 4c. Now, two oppositely twisted forms are denoted by δ' and λ' as shown in Fig. 4a. Of course, it is not necessary for the explanation of the optical activity of complexes with optically active ligands to take into account any puckering of chelate rings.[22] However, dissymmetric electron distributions around the coordinated atoms, if present, could be the main origins of ligand field Cotton effects as in the treatment of the simple molecular orbital theory.[23] Since the equatorial conformations of the C_α-substituents are considered to be the preferred forms from the observations in propylenediamine chelate rings (Fig. 4c), δ'-conformation may be assigned to the predominant form in both the chelate rings of L-α-amino acid-amide and -amidate in the complexes in solution as shown in Fig. 4b.

The ligand field CD bands of the bis(L-α-amino-acid-amidato) complexes of copper(II), nickel(II) and palladium(II) have predominantly negative sign over-all.[6,15] Such a CD spectral correspondence between d^8 spin paired and d^9 complexes of bis-chelated square planar structure may be also inferred from Liehr's theory.[23] However, a possibility of direct interactions between the C_α-substituents and the metal chromophores as a source of the Cotton effects cannot be ruled out. Recently, it has been reported[24] that the mono- and bis-type complexes of palladium(II), platinum(II) and gold(III) with (−)-propylenediamine and (−)-cyclohexanediamine reveal predominantly positive CD components in the ligand field band regions, where the ligands coordinate in λ-conformations. Thus, L-α-amino acidate, L-α-amino acid-amide and -amidate and (+)-propylenediamine as bidentate ligands seem to generally give the same sign to the Cotton effects caused by a particular d–d transition.

Now, whether (α) the puckerings of chelate rings or (β) the dispositions of C_α-substituents are the main origins of the Cotton effects? As shown in Figs. 5a and 5b, Wellman *et al.*[4] and Martin *et al.*[5] have applied oppositely signed spaces to L-α-amino acidato copper(II) complexes and explained their Cotton effects. This contradiction is resulted from the fact that they have simply regarded the different origin, (α) or (β), as the main source of the Cotton effects. Both explanations could revive even when each of the two spaces is applied to the models of the complexes with δ'- or λ'-conformations. It is to be noted, however, that the visible absorption band of any of these copper(II) complexes would possibly be the overlap of four components, that different origins would possibly be effective to different CD components, and consequently that such an alternately (+)- and (−)-signed space as the octant one for the n–π^* transition of ketones should be determined for a particular transition rather than for a particular geometry of the molecules. Indeed, it is in question whether the main positive CD components of the copper(II) complexes with L-prolinate, L-proline-amide and -amidate, and L-histidine amide[15] and the main negative ones of the corresponding copper(II) complexes with the other simple L-α-amino acid derivatives (like L-alanine derivatives) might be assigned to the same d–d transition or not. More investigations seem to be necessary to answer these questions.

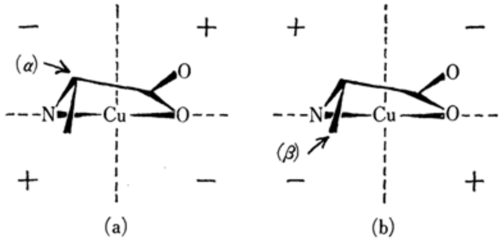

Fig. 5. (a) Wellman's and (b) Martin's spaces applied to the proposed model of L-amino acidato complex.
The signs are given to the front octants or sectors which contain the ligand. (α) and (β) indicate the supposed origins for the negative Cotton effects.

The CD spectra of the R-type complexes are considerably influenced by changing the solvent. However, a general pattern of the curve for each the complex is well retained as may be seen in Figs. 2 and 3. This fact may point out that the change of solvent gives rise to little changes in the equilibria between the chelate ring conformations (inclined to δ') and between the geometrical isomers (presumably inclined to trans).

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[21] H. C. Freeman, M. R. Snow, I. Nitta and K. Tomita, *ibid.*, **17**, 1463 (1964).

[22] The puckering found in the glycinato or the glycylglycinato chelate ring is somewhat smaller in size, and might be more flexible, than that of ethylenediamine chelate ring. CD data for the copper(II) complexes with some tetradentate ligands seem to reveal such a somewhat ambiguous nature of the conformations of the ligands; Ref. 5, and M. Parris and A. E. Hodges, *J. Am. Chem. Soc.*, **90**, 1909 (1968).

[23] A. D. Liehr, *J. Phys. Chem.*, **68**, 3629 (1964).

[24] H. Ito, J. Fujita and K. Saito, This Bulletin, **40**, 2584 (1967).

It is interesting to examine the relative order of the dissymmetric field strengths of the bidentate ligands in the complexes. The following orders are easily derived from the CD or the rotatory dispersion data:

L-alaaH $<$ L-leuaH $<$ L-valaH

for the B-type,

L-alaa$^-$ $<$ L-leua$^-$ $<$ L-vala$^-$

for the R-type, and

L-ala$^-$ $<$ L-leu$^-$ $<$ L-val$^-$

for the amino acidato copper(II) complexes.[3,4] From these orders, the relative dissymmetric field strengths seem to be determined by the mother amino acids. In addition the relative order, L-amino acidate $\sim$ L-amino acid amide $<$ L-amino acid amidate, is apparently observed for a series of the bis-type copper(II) complexes[3,4] with the ligands derived from a particular amino acid, and considered to originate from the different covalency in the coordination squares or from the different degree of the puckerings of the chelate rings.

4) CD Behavior of the Complexes with L-Proline-Amide, -Amidate and L-Prolinate. As shown in Fig. 1, the CD spectrum of Cu(L-proaH)$_2$SO$_4$ in the aqueous solution is markedly different from those of the corresponding species with the other four L-amino acid amides. It has been known[3] that Cu(L-pro)$_2$ and Cu(L-hypro)$_2$ reveal more distinct ligand field CD bands than those of the corresponding species with the other simple L-amino acidates. The CD spectrum of Cu(L-proaH)$_2$SO$_4$ is very similar to that of Cu(L-pro)$_2$ in aqueous solution. Cu(L-proa)$_2$ also reveals a very specific CD behavior, although its negative CD components are dominant as those of the other R-type complexes (Figs. 2 and 3). Similar behavior has been observed in Ni(L-proa)$_2$, too.[15] A common nature in the CD behavior among Cu(L-proa)$_2$, Cu(L-proaH)$_2{}^{2+}$ and Cu(L-pro)$_2$ could be derived from the fact that a positive component of the former complex in the dimethylformamide solution is so conspicuous as those of the latter two in the aqueous solutions (Fig. 3).

From these considerations, it may be possible to say that the dissymmetric fields produced near the Cu(N)$_4$ chromophores are specified by the coordinated L-proline-amide, -amidate and L-prolinate.[25] The specificity might potentially be derived from the following origins: i) asymmetry of the pyrrolidine nitrogen;[3] ii) direct interaction between the chromophore and one of the two hydrogen atoms attached to the fifth carbon atom of the pyrrolidine ring, which projects over the coordination square as shown in Fig. 6; and iii) fixed form of the chelate ring, which might be forced by the pyrrolidine ring together with the C–CO–O, C–CN–O or C–CO–N moiety. It may be said that the data for bis(*N*-methyl-L-prolinato)copper(II) show the effectiveness of i) or ii).[5] On the other hand, the CD behavior of Cu(L-proa)$_2$, which is considerably different from that of Cu(L-pro)$_2$ or Cu(L-proaH)$_2{}^{2+}$, may be considered to show the effectiveness of iii). As a consequence of iii), asymmetry of the electron distribution near the amidato nitrogen (or the coordinated carboxyl oxygen) should be noted. This effect cannot be simply ruled out, since the charge transfer band of Cu(L-proa)$_2$ (presumably, metal-amidate in nature), for example, occurs at rather lower wave number's (Fig. 3).

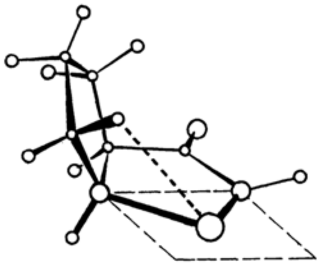

Fig. 6

5) The Near-Ultraviolet Absorption Band of R-type Complex. All the R-type complexes

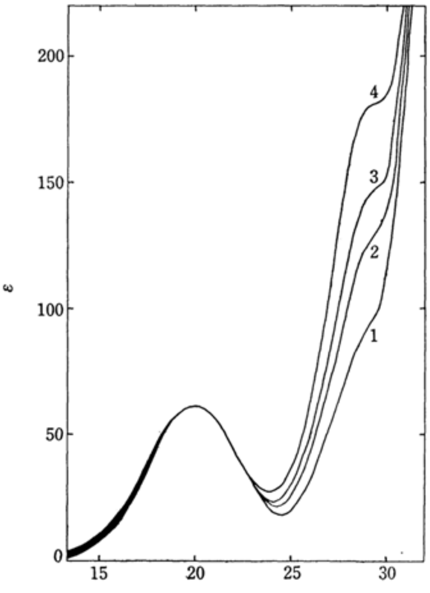

Fig. 7. Absorption spectrum of Cu(L-alaa)$_2$ in ethanol.
1: 8.4 mF 2: 2.8 mF 3: 1.4 mF 4: 0.7 mF

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[25] On the basis of this specification and the presumed trans structure of Cu(L-proa)$_2$, it seems to be rather unreasonable to assign cis structure to Cu(L-pro)$_2$ in water; R. D. Gillard, *Inorg. Chim. Acta Rev.*, **1967**, 69.

exhibit another kind of absorption bands (Band II) at about 29000 cm^{-1} in the alcoholic solutions (Table 2 and Figs. 2 and 7). (Band II seems to be almost embedded in the charge transfer band in the spectrum of the L-proline amidato complex.) These bands disappear in aqueous solution or in solid state, though the disappearance is not perfect in aqueous solution. As may be seen in Fig. 7, the Band II of Cu(L-alaa)_2 in the ethanolic solution is accompanied with the increase of intensity when the solution is diluted. Similar concentration dependence of Band II was observed for every R-type complex in the methanolic and aqueous solutions. The Band II cannot be, therefore, considered to originate in any association among the complexes. Cotton effects of the R-type complexes are negligible at about 29000 cm^{-1} as shown in Figs. 2 and 3. As a consequence, if Band II might be assigned to one of d–d transitions, it should be to $(z^2)\rightarrow(x^2-y^2)$ transition from a theoretical consideration.[6] Band II of Cu(L-alaa)_2 was, however, inclined to shift to lower wave number's when the solvent was changed from water to methanol, and to ethanol.[15] This behavior of the Band II cannot be consistently interpreted on the basis of the band assignment. It may be concluded, therefore, that Band II cannot be assigned to any d–d transition.

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