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Metal Complexes of Amino Acids. II.[1] The Absorption Spectra of Geometrical Isomers of Copper(II) Complexes

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The geometrical structures of bis(α-amino-acidato)copper(II) complexes have been determined from the data of diffuse reflectance spectra (α-amino-acid = glycine, L- and DL-α-alanine, L- and DL-valine, L- and DL-threonine, L- and DL-isoleucine and α-aminoisobutyric acid). It has been shown that pairs of cis(N) and trans(N) isomers exist in glycinato and valinato complexes. It has been clarified that the other amino-acidato complexes studied exist either only in the cis(N) form or only in the trans(N) form; that is, the needle and the scaly complexes of DL-alanine, the complexes of DL- and L-threonine, and the complex of α-aminoisobutyric acid exist only in the trans(N) form, while the complexes of L- and DL-isoleucine exist only in the cis(N) form.

1) Part I of this series: T. Yasui, This Bulletin, 38, 1746 (1965).

The well-known bright-blue crystal of copper(II) glycinate has been shown through X-ray analyses[2] to consist of the bis(glycinato)copper(II) complex, which has a cis(N) configuration involving the two nitrogen atoms of the two coplanar glycinate ligands. The other bluish-violet isomer of bis-(glycinato)copper(II) had been discovered by Mauthner and Suida[3]; it has been assumed to be the trans(N) isomer from a comparison of its infrared absorption spectrum with those of the corresponding trans isomers of bis(glycinato)platinum-(II) and -palladium(II).[4]

For other amino acids, however, no pair of the cis and trans isomers of a copper(II) complex has been known. All copper(II) amino-acid complexes the structures of which were determined by X-ray analysis, had the trans configuration except for the above-mentioned cis glycinato complex. Recently Hooper et al.[5] suggested, from their infrared study, that bis(DL-isoleucinato)copper(II) monohydrate has the cis structure. One of the purposes of the present investigation is to explore other pairs of the cis-trans isomers of copper(II) complexes.

We have shown already by a circular dichroism study[1,6] that a broad visible d→d absorption band of the bis(amino-acidato)copper(II) complex consists of four split components. The difference in symmetry between the cis and the trans isomers will be reflected in the behavior of the d→d absorption bands. In the present paper, the diffuse reflectance spectra of the powdered copper(II) complexes in the region from the near infrared to visible will be reported on, and the geometrical configurations of the complexes will be discussed.

Experimental

Measurement.—The measurements of diffuse reflectance spectra were made by a Hitachi EPU-2A spectrophotometer with a diffuse reflectance attachment. The samples were prepared by grinding the complexes as finely as possible in a porcelain mortar and then in an agatic one until no change appeared in the intensity of the spectra. Magnesium oxide was employed as the reference.

Materials.—The copper(II) complexes with amino acids and with amino acid derivatives were prepared from copper(II) hydroxide by a method similar to that of Abderhalden and Schnitzler.[7]

The *cis*-bis(glycinato)copper(II) complex and the bis(amino-acidato)copper(II) complexes of DL- and L-alanine, DL- and L-valine, DL- and L-threonine, DL-α-amino-*n*-butyric acid, and α-aminoisobutyric acid were recrystallized from aqueous alcohol. The bluish-violet glycine complex was obtained by the method of Mauthner and Suida,[3] and the scaly crystals of the DL-alanine complex by following the directions of Gol'braikh.[8]

Table I. Chemical analyses of the complexes

Complex*	C, %		H, %		N, %		H_2O, %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
cis-[Cu gly_2]·H_2O	23.04	22.70	3.78	3.80	13.37	13.24	7.58	7.84
[Cu gly_2]·H_2O (scaly)	22.91	22.70	3.85	3.80	13.39	13.24	7.94	7.84
[Cu(DL-ala)$_2$]·H_2O (needle)	30.06	30.06	4.88	5.05	11.45	11.69	7.20	7.00
[Cu(DL-ala)$_2$] (scaly)	30.32	30.06	5.02	5.05	11.44	11.69	—	—
[Cu(DL-val)$_2$]	40.84	40.60	6.81	6.81	9.53	9.47	—	—
[Cu(DL-thr)$_2$]	32.25	32.05	5.37	5.38	9.32	9.35	—	—
[Cu(L-isoleu)$_2$]·H_2O	44.08	44.22	7.31	7.44	8.60	8.60	5.38	5.27
[Cu(DL-isoleu)$_2$]·H_2O	44.51	44.22	7.27	7.44	8.64	8.60	5.28	5.27
[Cu(DL-Etgly)$_2$]	36.05	35.88	5.99	6.03	10.50	10.46	—	—
[Cu(Me_2gly)$_2$]	35.98	35.88	6.03	6.03	10.30	10.46	—	—
[Cu(ph_2edda)]·H_2O	55.28	55.44	4.67	4.66	7.23	7.19	4.46	4.42
[Cu(ph_2edpa)]·H_2O	57.68	57.47	5.36	5.32	6.96	6.70	4.41	4.13
[Cu(ediba)]·$3H_2O$	40.52	40.88	6.12	6.18	9.54	9.54	15.16	15.54
Cu(en)SO_4·$2H_2O$	9.26	9.39	4.64	4.74	10.20	10.95	—	—

* gly=glycinate, ala=α-alaninate, val=valinate, thr=threoninate, isoleu=isoleucinate, Etgly=α-amino-*n*-butyrate, Me_2gly=α-aminoisobutyrate, ph_2edda=ethylene-bis(α-iminophenylacetate), ph_2edpa=ethylene-bis(α-iminophenylpropionate), ediba=ethylene-bis(α-iminoisobutyrate), en=ethylenediamine.

2) H. C. Freeman, M. R. Snow, I. Nitta and K. Tomita, *Acta Cryst.*, **17**, 1463 (1964); K. Tomita and I. Nitta, This Bulletin, **34**, 286 (1961).
3) J. Mauthner and W. Suida, *Monatsh.*, **11**, 373 (1890).
4) T. J. Lane, J. A. Durkin and R. J. Hooper, *Spectrochim. Acta*, **20**, 1013 (1964).
5) R. J. Hooper, T. J. Lane and J. L. Walter, *Inorg. Chem.*, **3**, 1568 (1964).
6) T. Yasui, J. Hidaka and Y. Shimura, *J. Am. Chem. Soc.*, **87**, 2762 (1965).
7) E. Abderhalden and E. Schnitzler, *Z. physiol. Chem.*, **163**, 94 (1927).
8) Z. E. Gol'braikh, *Zhur. Neorg. Khim.*, **1**, 1739 (1956).

The copper(II) complexes of DL- and L-isoleucine, ethylene-bis(α-iminophenylacetic acid)[9a] and ethylene-bis(α-iminophenylpropionic acid)[9a] were recrystallized from hot water, and that of ethylene-bis(α-iminoisobutyric acid),[9b] from aqueous acetone. An ethylenediamine compound, $Cu(en)SO_4 \cdot 2H_2O$, was obtained by the method of Pfeiffer and Glaser[10] and recrystallized from aqueous alcohol.

The results of the chemical analyses are listed in Table I for all of the complexes obtained.

The preparations of the remaining complexes have already been reported in a previous report of this series.[1]

Results and Discussion

The spectral curves obtained by the diffuse reflectance measurements are shown in Figs. 1—5. The absorption spectrum of the glycine complex in an aqueous solution shows only one broad band and gives little information about the geometrical structures. Moreover, the cis and the trans isomers give identical spectra in an aqueous solution, probably reaching a cis-trans equilibrium mixture by the rapid rearrangement of the ligands.

The spectral difference between the bright blue *cis*-[Cu gly_2]$\cdot H_2O$ and the bluish-violet [Cu gly_2]$\cdot H_2O$, which can not be observed in an aqueous solution, definitely appears in the solid states, as may be seen in Fig. 1. The spectrum of the bluish violet [Cu gly_2]$\cdot H_2O$ is similar to that in an aqueous solution, but the *cis*-[Cu gly_2]$\cdot H_2O$ in the solid state has the peak at a longer wavelength than that of the bluish-violet form and an accompanying shoulder on the longer wavelength side. This fact indicates that the structure of *cis*-[Cu gly_2]$\cdot H_2O$ in the crystal is considerably different from that in an aqueous solution, and that the symmetry of the complex molecule is rather lowered. This agrees very well with the results of the X-ray study of the *cis*-[Cu gly_2]$\cdot H_2O$.[2] The spectra of the ethylene-bridged copper(II) complexes with cis structures are similar to that of the *cis*-[Cu gly_2]$\cdot H_2O$ (Fig. 2). The spectrum of the bluish-violet [Cu gly_2]$\cdot H_2O$ coincides exactly with that of *trans*-[Cu(DL-Etgly)$_2$], the structure of which has been determined by X-ray analysis.[11] It may be concluded, therefore, that the bluish-violet [Cu gly_2]$\cdot H_2O$ is the trans form. This conclusion is also consistent with the studies of infrared spectra.[4,12]

Another difference between the spectrum of *cis*-[Cu gly_2]$\cdot H_2O$ and that of bluish-violet [Cu gly_2]$\cdot H_2O$ lies in their intensities. The maximum absorption of the former is more intense than that of the latter, although not quite definitely so, since the intensities of diffuse reflectance spectra depend on the particle size of the samples. According to Belford and Yeranos,[13] the intensities of the d→d absorption of copper(II) complexes are enhanced by the cis-structure or the strong interaction of the solvent to the fifth and/or sixth coordination positions.

In Fig. 3 the curves of [Cu(DL-ala)$_2$]$\cdot H_2O$ (needle) and of [Cu(DL-ala)$_2$] (scaly) almost coincide with that of the *trans*-[Cu(L-ala)$_2$], in which the

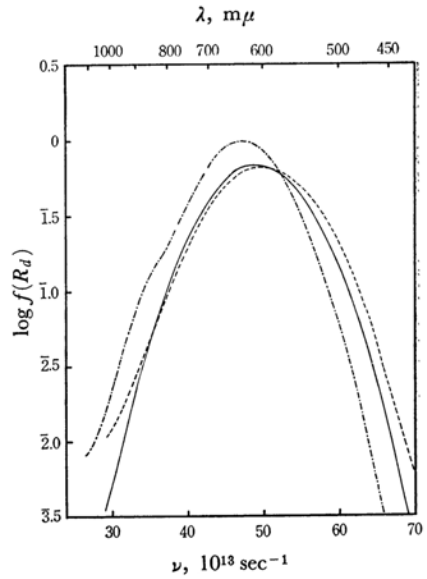

Fig. 1. The diffuse reflectance curves of *cis*-[Cu gly_2]$\cdot H_2O$ (-·-·-), bluish violet [Cu gly_2]$\cdot H_2O$ (——) and *trans*-[Cu(DL-Etgly)$_2$] (- - -).

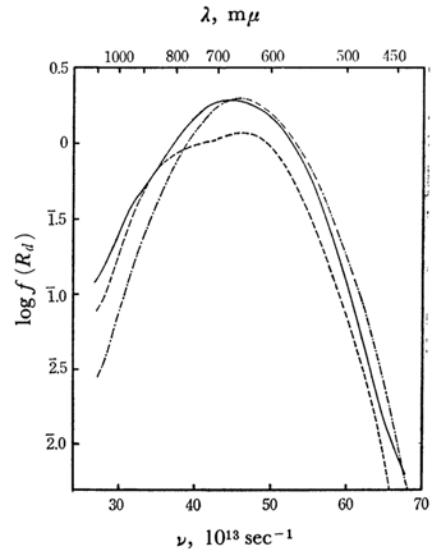

Fig. 2. The diffuse reflectance curves of [Cu-(ph_2 edda)]$\cdot H_2O$ (——), [Cu(ph_2 edpa)]$\cdot H_2O$ (-·-·-), and $Cu(en)SO_4 \cdot 2H_2O$ (- - -).

9) a) N. Schlesinger, *Ber.*, **45**, 1486 (1912); b) ibid., **44**, 1135 (1911).
10) P. Pfeiffer and H. Glaser, *J. prak. Chem.*, **151**, 134 (1938).
11) A. J. Stosick, *J. Am. Chem. Soc.*, **67**, 362 (1945).
12) K. Tomita, This Bulletin, **34**, 280 (1961).
13) R. L. Belford and W. A. Yeranos, *Mol. Phys.*, **6**, 121 (1963).

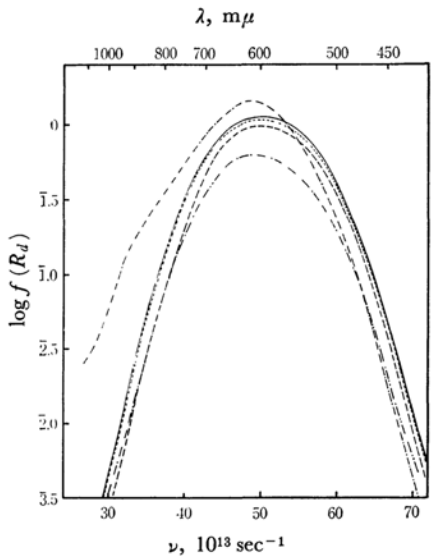

Fig. 3. The diffuse reflectance curves of [Cu(DL-ala)$_2$]·H_2O (——), [Cu(DL-ala)$_2$] (·····), [Cu(L-ala)$_2$] (– – –), [Cu(L-val)$_2$]·H_2O (–·–·) and [Cu-(DL-val)$_2$] (–···–···).

ligand L-alanine is coordinated to copper(II) in a trans planar configuration.[14] Therefore, it may be suggested that both the DL-alanine complexes take the trans structure, although their crystal forms and colors are different. In the valine complexes an interesting fact has been found; the spectrum of [Cu(L-val)$_2$]·H_2O corresponds to that of *cis*-[Cu gly$_2$]·H_2O, and the spectrum of [Cu-(DL-val)$_2$], to that of bluish-violet [Cu gly$_2$]·H_2O or *trans*-[Cu(DL-Etgly)$_2$] (Fig. 3). Moreover the band of [Cu(L-val)$_2$]·H_2O is more intense than that of [Cu(DL-val)$_2$]. From these facts, it may be concluded that the complex with L-valine is the cis form, and that with DL-valine is the trans form. Because of their different geometrical structures, it is possible that the interaction between the terminal isopropyl groups of the coordinated valines is smaller in the trans than in the cis complex of DL-valine, but it is smaller in the cis than in the trans complex of L-valine.

Similarly, it may be concluded from Fig. 4 that the complexes of isoleucine have the cis configuration, and that those of threonine have the trans configuration. The band of [Cu(DL-isoleu)$_2$]·H_2O has a higher intensity than that of [Cu(L-isoleu)$_2$]·H_2O; this may be interpreted as partly due to the aquo-ligand coordinated strongly to the copper atom and partly due to the cis structure.[13] The conclusion that [Cu(DL-isoleu)$_2$]·H_2O is the cis form also agrees with the conclusion which has been suggested from the infrared spectra.[5] The spectral behaviors of [Cu(DL-thr)$_2$] and [Cu(L-thr)$_2$]·

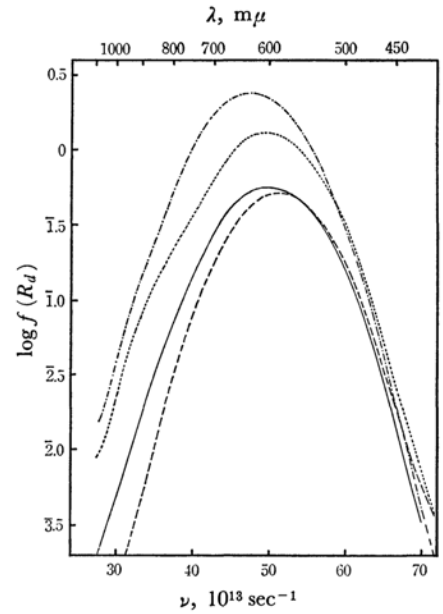

Fig. 4. The diffuse reflectance curves of [Cu(DL-(thr)$_2$] (——), [Cu(L-thr)$_2$]·H_2O (– – –), [Cu-(DL-isoleu)$_2$]·H_2O (–·–·) and [Cu(L-isoleu)$_2$]·H_2O (·····).

H_2O are almost identical with those of *trans*-[Cu(DL-Etgly)$_2$] and [Cu(DL-val)$_2$]; they show that they have the trans configuration.

The spectra of [Cu(Me$_2$gly)$_2$] and of the complex of isobutyric derivative, [Cu(ediba)]·3H_2O, show a different trend from those of the complexes with familiar amino acids mentioned above; that is, they show a shoulder on the shorter wavelength

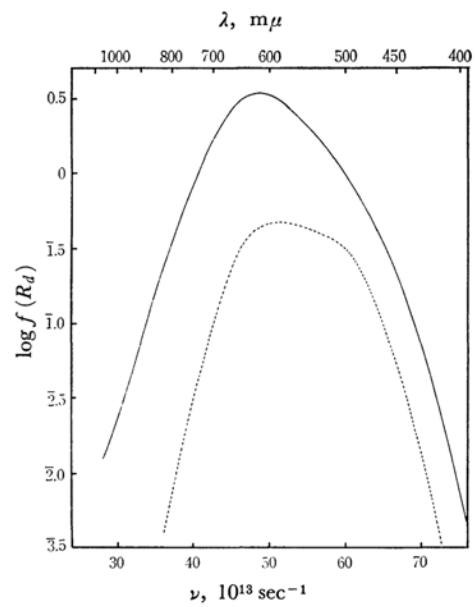

Fig. 5. The diffuse reflectance curves of [Cu-(ediba)]·3H_2O (——) and [Cu(Me$_2$gly)$_2$] (·····).

14) C. G. Vonk et al., quoted by C. Dijkgraaf, *Spectrochim. Acta*, **20**, 1227 (1964).

Table II. Colors and geometrical structures of the complexes

Complex	Color	Geometrical structure
$[Cu\ gly_2]\cdot H_2O$ (scaly)	Bluish violet	trans
$[Cu(DL\text{-}ala)_2]\cdot H_2O$ (needle)	Blue	trans
$[Cu(DL\text{-}ala)_2]$ (scaly)	Bluish violet	trans
$[Cu(L\text{-}val)_2]\cdot H_2O$	Blue	cis
$[Cu(DL\text{-}val)_2]$	Bluish violet	trans
$[Cu(L\text{-}thr)_2]\cdot H_2O$	Blue	trans
$[Cu(DL\text{-}thr)_2]$	Bluish violet	trans
$[Cu(L\text{-}isoleu)_2]\cdot H_2O$	Bluish violet	cis
$[Cu(DL\text{-}isoleu)_2]\cdot H_2O$	Bright blue	cis
$[Cu(Me_2gly)_2]$	Violet	trans

side (Fig. 5). Graddon and Munday[15] suggested, from the shoulder of $[Cu(Me_2gly)_2]$ on the shorter wavelength side, that the complex molecule has a purely tetragonal planar structure. The lower intensity of the band of this complex may be due to its trans-structure.

The geometrical structures of the bis(amino-acidato)copper(II) complexes which have been determined from the data of diffuse reflectance spectra are summarized in Table II.

15) D. P. Graddon and L. Munday, *J. Inorg. Nucl. Chem.*, **23**, 231 (1961).