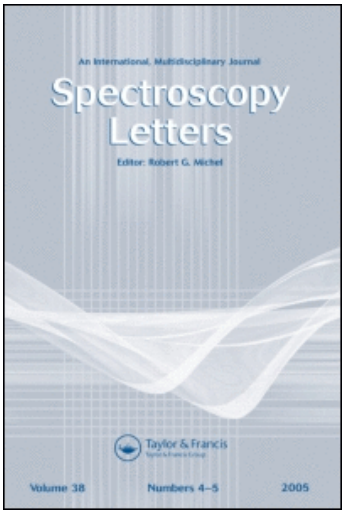

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Spectroscopic and Structural Studies of Complexes of Copper (II) with L-Isoleucine and L-Leucine

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SPECTROSCOPIC AND STRUCTURAL STUDIES OF COMPLEXES OF COPPER(II) WITH L-ISOLEUCINE AND L-LEUCINE

Key words: electronic absorption spectra, bis(amino acidato)copper(II), ligand field theory and structural studies

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ABSTRACT

The electronic absorption spectrum of bis(L-isoleucinato)copper(II) monohydrate has been measured.Four absorption bands appear at about 9600, 15325, 16145 and 17963cm^{-1} respectively. The experimental results are in agreement with the values calculated with Ligand Field Theory (LFT) and radial wave function of nonfree copper (II). In particular, the spectra of some bis(amino acidato) copper(II) complexes are herein compared with each other as an important work of spectroscopic and structural study.

INTRODUCTION

Many transition-metal ions play important roles in the body of the living things. They enter cells by means of the ferry of amino acids. So it has great biological significance to study the coordination compounds

of copper(II) with amino acids. In previous papers [1], we have reported electronic absorption spectra of some complexes of copper(II) and nickel (II) with amino acids.Our present investigation is undertaken to provide a series of well-characterized model compounds of metal-proteins.

In this paper,electronic absorption spectrum of bis(L-isoleucinato) copper(II) monohydrate (abbreviated $Cu(L\text{-}Ile)_2 \cdot H_2O$) is recorded, and compared with those of bis(L-valinato)copper(II) monohydrate(abbreviated $Cu(L\text{-}Val)_2 \cdot H_2O$), bis(L-leucinato)copper(II)(abbreviated $Cu(L\text{-}Leu)_2$) and other bis(amino acidato)copper(II) complexes.It is thought meaningful to explore correlation between features appearing in alternative spectra of Cu(II)-amino acid complexes and their structures. Intensity variation in diffuse reflectance spectra [2,3],optical activity effects in CD spectra [4],Cu-N and Cu-O stretching modes in IR spectra [5] and ESR spectra [6] of bis(amino acidato)copper(II) complexes have been used to prejudge cis and trans configurations. Some workers have, recently, reported crystal structure for $Cu(DL\text{-}Ile)_2$, whose coordination geometry was compared with $Cu(L\text{-}Ile)_2.H_2O$ and examined with the asist of ESR spectrum [7]. Our work makes it possible to obtain more structural information from electronic absorption spectrum than those spectra mentioned above. The complexes in this paper all have very low symmetries.

EXPERIMENTAL

Bis(L-isoleucinato)copper(II) monohydrate was prepared by reaction of copper carbonate with L-isoleucine in molar ratio in 1: 2 proportion. After slow evaporation of the aqueous solution at room temperature, deep blue crystals were obtained.

The anhydrous complexes bis(L-leucinato)copper(II) crystallized as six-sided blue plates which were separated from a solution containing $CuCl_2 \cdot 2H_2O$, L-leucine, and urea in the ratio 1: 2: 1, by urea hydrolysis technique [8].

Elemental analysis were measured using a Perkin-Elmer 240 C and the observed values were found approximately equal to calculated values.

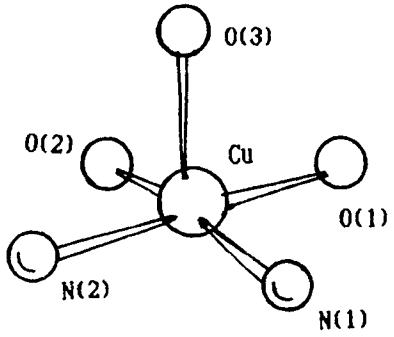

FIG. 1. Crystal structure of Cu $(L\text{-}Ile)_2 \cdot H_2O$.

Electronic absorption spectrum of each complex was recorded in the region from 6000-30000cm^{-1}, but only the region from 6000 to about 24000 cm^{-1} is generally drawn in the figures.

RESULTS AND DISCUSSION

Description of the Structures In the crystals of $Cu(L\text{-}Ile)_2 \cdot H_2O$, copper(II) ion coordination as a distorted square pyramid with one water molecule occupying an axial position [9] is clearly seen in Fig.1. Two isoleucine molecules cis coordinate to copper atoms. The data of crystal structure [9] (Tab. 1) exhibit a very flattened tetrahedron, neither a square nor a tetragon, which is produced by equatorial N_2O_2 ligation. It could be thought that the cis conformation of $Cu(L\text{-}Ile)_2 \cdot H_2O$ allows a more extensive hydrogen bonding system.

The copper ions in the crystal of $Cu(L\text{-}Val)_2 \cdot H_2O$ have coordination similar to $Cu(L\text{-}Ile)_2 \cdot H_2O$. It should be noted, simply according to the θ angles of N_1, N_2, O_1 and O_2 and bonding length of $Cu\text{-}O_5$ [10] (Tab.1), that the latter is even more distorted from square pyramid.

TABLE 1

The data of the crystal structure of $Cu(L\text{-}Ile)_2 \cdot H_2O$

R, θ, Φ	O(3)	N(2)	N(1)	O(1)	N(2)
R (Å)	2.475	1.995	1.989	1.948	1.953
θ (deg.)	0	86.9	85.1	97.5	111.7
Φ (deg.)	—	0	98.6	182.1	277.2

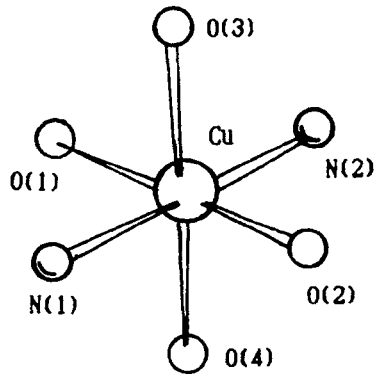

FIG. 2. Crystal structure of Cu $(L\text{-}Leu)_2$.

A drawing of the structure of $Cu(L\text{-}Leu)_2$ which can show the nearest neighbouring atoms around copper atom is present in Fig.2. The structure [8] consists of tetragonally coordinated Cu(II) ions located in isolated sheets. Equatorial N_2O_2 ligation is provided by trans coordination of two L-leucine molecules, while axial Cu-O ligation by two neighbouring amino acids completes metal(II) ion coordination and links CuL_2 units to form carboxylate-bridged sheets of Cu(II) ions. Intermolecular hydrogen bonds further link the CuL_2 units within each sheet. Coordination of the polar ends of L-leucine with Cu(II), in return, allows the nonpolar side chains to align, and hydrophobic regions are therefore created. Double layers of this type, which do not exist in the crystals of $Cu(L\text{-}Ile)_2 \cdot$

TABLE 2

The data of the crystal structure of $Cu(L\text{-}Leu)_2$

R, θ, Φ	O(1)	O(2)	O(3)	O(4)	N(1)	N(2)
R (A°)	1.960	1.960	2.629	2.749	1.989	1.996
θ (deg.)	87.3	92.9	0.0	173.98	85.9	99.5
Φ (deg.)	275.8	95.9	—	—	0.0	174.6

TABLE 3

The crystal field parameters of $Cu(L\text{-}Ile)_2 \cdot H_2O$ and $Cu(L\text{-}Leu)_2$

parameters	$Cu(L\text{-}Ile)_2 \cdot H_2O$	$Cu(L\text{-}Leu)_2$	parameters	$Cu(L\text{-}Ile)_2 \cdot H_2O$	$Cu(L\text{-}Leu)_2$
$\overline{\mu}$ (Debye)	1.11480	1.10133	a_1	0.58494	0.59203
t	0.03754	0.02806	a_2	0.63847	0.64621
Ω(Hartree)	0.16497	0.19929	$\langle r^2 \rangle$ (a.u)	2.01531	2.32611
N	0.9980	0.9760	$\langle r^4 \rangle$ (a.u)	11.07537	15.06065
p^2	1.56572	1.56829	$\langle r^{-3} \rangle$(a.u)	5.75908	5.42708
p^4	1.93911	1.88056	B (cm^{-1})	1019	954
ζ_1	5.87170	5.76140	C (cm^{-1})	3480	3265
ζ_2	1.86418	1.73281	ζ_{3d}(cm^{-1})	558	520

Where μ is dipole moment of ligand (in Debye), t is the ratio of dipole length and bond length, Ω is the so-called scale of nonfreedom, which is a parameter variable to describe the deviation from free ions.

TABLE 4

The electronic absorption spectra of $Cu(L\text{-}Val)_2 \cdot H_2O$, $Cu(L\text{-}Ile)_2 \cdot H_2O$ and $Cu(L\text{-}Leu)_2$

	Calc.			Obs.		
Maxima (cm^{-1})	a	b	c	a	b	c
$\overline{\nu_1}$	9319	9887	10169	9440	9600	10000
$\overline{\nu_2}$	13859	14428	15300	13285	15325	15276
$\overline{\nu_3}$	14821	15625	16653	15296	16145	16222
$\overline{\nu_4}$	16654	17044	19083	17183	17963	19430

Where a, b and c are attached to the values of $Cu(L\text{-}Val)_2 \cdot H_2O$, $Cu(L\text{-}Ile)_2 \cdot H_2O$ and $Cu(L\text{-}Leu)_2$ respectively.

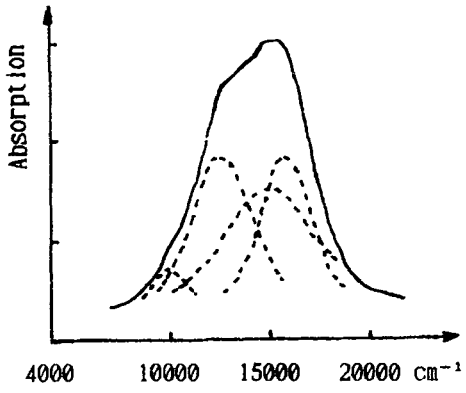

FIG. 3. Electronic absorption spectrum of $Cu(Gly)_2 \cdot H_2O$.

H_2O, are common to many structures of metal-amino acid complexes [8, 11] though the packing manners are slightly different. We have to attribute this variation to the effect of amino acid residues. It has attracted our attention that slight alteration of side chain of amino acids leads the structure of metal amino acid complex to change considerably.

Theoretical Calculation and Spectroscopic Results We now list the data of crystal structures of $Cu(L\text{-}Ile)_2 \cdot H_2O$, $Cu(L\text{-}Val)_2 \cdot H_2O$ and $Cu(L\text{-}Leu)_2$ in Tab.1 and Tab.2 in globe coordinate, respectively, and choose $Cu\text{-}O_3$ as Z axis. The approximate symmetry of Cu ion is C_1 (Fig.2, Tab.2) for $Cu(L\text{-}Leu)_2$, and C_1 (Fig.1, Tab.1) for $Cu(L\text{-}Ile)_2 \cdot H_2O$. According to Tab.1, Tab.2, the environment of Cu(II), and the coordinate system we have taken, the original data files can be set up. The parameters of the crystal field and electronic energy level are calculated using the PLFT [11]. The values are shown in Tab.3 and Tab.4, respectively. The observed values in Tab.4 are a issue of computer resolution.The results which are calculated assuming strong field because of very low symmetry, coincide well with the experimental values. We, here, have chance to correct a mistake in one of our previous communications [12], where the resolution error(only about 0.01) is not adequate. As a rule, we limit the error as

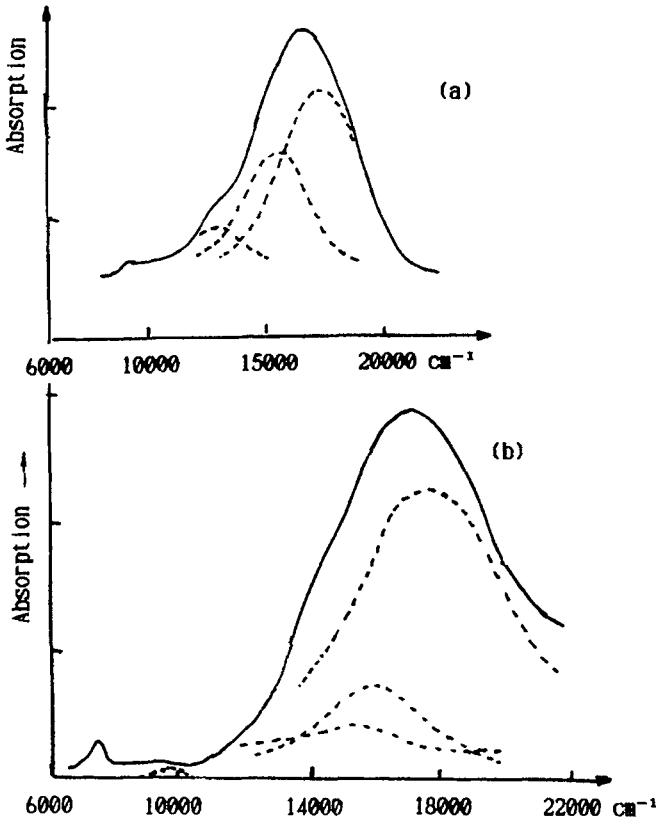

FIG. 4. Electronic absorption spectra of $Cu(L\text{-}Val)_2 \cdot H_2O$ (a) and $Cu(L\text{-}Ile)_2 \cdot H_2O$ (b). There is no correlation between their intensities.

much as possible. The resolution error above can, in fact, reach 0.001, thus correct resolved spectra are given in this paper.

The room temperature electronic absorption spectra of Cu (II) cis complexes with Gly [13], L-Val [14] and L-Ile, and trans complex with L-Leu are shown in Fig.3, Fig.4 and Fig.5. Each spectrum was analyzed into Gaussian components on an IBM PC/XT computer with a program of Fan Jifa et al [15]. Band maxima ($\overline{\nu}$) and absorptivities (ε) of nearly equimolar

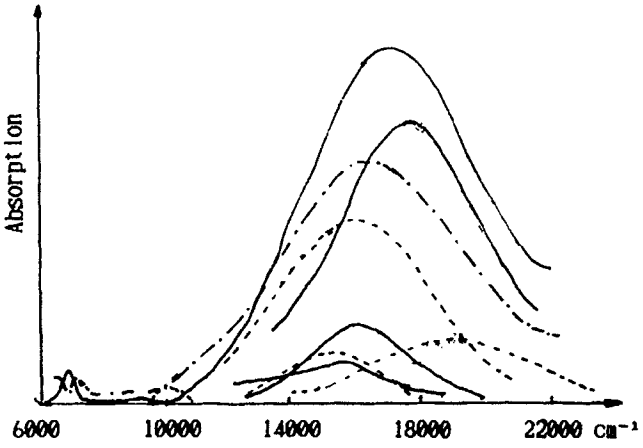

FIG. 5. Electronic absorption spectra of $Cu(L\text{-}Ile)_2 \cdot H_2O$ (the solid lines) and $Cu(L\text{-}Leu)_2$ (the dotted lines). They were recorded under the same condition and drawn in nearly the same scale.

$Cu(L\text{-}Ile)_2 \cdot H_2O$ and $Cu(L\text{-}Leu)_2$ are collected in Tab.5 (Each spectrum in this paper contains four peaks located at $\overline{\nu}_1$, $\overline{\nu}_2$, $\overline{\nu}_3$ and $\overline{\nu}_3$, orderly rowed up from low energy to high energy).

After resolved, the spectra of $Cu(L\text{-}Val)_2 \cdot H_2O$ and $Cu(L\text{-}Ile)_2 \cdot H_2O$ (Fig.4) resemble each other, particularly in the intensity distribution of band maxima $\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \varepsilon_4$, since both of the cis complexes have similar significantly distorted square pyramidal coordination which have have just been described. Considerably intense peaks ($\overline{\nu}_1$, $\overline{\nu}_2$ and $\overline{\nu}_3$) positioned on the left of the main peak ($\overline{\nu}_4$) are reminiscent of rather lowered symmetry from square pyramid. In fact, when calculating, we have regarded the symmetries as C_1 according to the data of the both crystal structures. additionally, apparent shifts to high energy with comparison between the absorption bands of $Cu(L\text{-}Ile)_2 \cdot H_2O$ and those of $Cu(L\text{-}Val)_2 \cdot H_2O$ (Fig.4) probably contain sizable contribution from more considerable

TABLE 5

The band maxima and intensities of $Cu(L\text{-}Ile)_2 \cdot H_2O$ and $Cu(L\text{-}Leu)_2$

Compound	$\bar{\nu}_1$	ε_1	$\bar{\nu}_2$	ε_2	$\bar{\nu}_3$	ε_3	$\bar{\nu}_4$	ε_4
$Cu(L\text{-}Ile)_2 \cdot H_2O$	9600	<0.2	15325	0.20	16145	0.61	17963	1.79
$Cu(L\text{-}Leu)_2$	10000	<0.2	15276	0.24	16222	1.14	19430	0.39

Where the unit for $\bar{\nu}_i$ (i=1-4) is cm^{-1}, and the values of ε_i are all approximate and relative.

TABLE 6

Electronic absorption spectral features in relation to ε_2 and ε_3

Compound	Coordination type	Feature	Ref.
$Cu(L\text{-}Val)_2 \cdot H_2O$	fivefold, cis	$\varepsilon_2 < \varepsilon_3$	14
$Cu(Gly)_2 \cdot H_2O$	sixfold, cis	$\varepsilon_2 > \varepsilon_3$	13
$Cu(L\text{-}Leu)_2$	sixfold, trans	$\varepsilon_2 < \varepsilon_3$	this paper

distortion. This tendency is different from what R. C. Rosenberg et al. reported for square planar Cu(II) [16].

Comparison of the absorption spectrum of $Cu(L\text{-}Ile)_2 \cdot H_2O$ with that of $Cu(L\text{-}Leu)_2$ (Fig.5) shows the former absorption is more strong. The intensity enhancement of d-d absorption spectrum could be explained [2] by the fact that $Cu(L\text{-}Ile)_2 \cdot H_2O$ is cis while $Cu(L\text{-}Leu)_2$ is trans. It is visible another difference between the two spectra lies in the position of peak $\bar{\nu}_4$. In the former spectrum, peak $\bar{\nu}_4$ falls below 18000 cm^{-1}, while for the latter, peak $\bar{\nu}_4$ goes beyond 19000cm^{-1}. The d-d electronic absorption bands of all the CuO_xN_y (x+y=5) complexes we have studied [1] exhibit the maximum $\bar{\nu}_4$ at not greater than 19000 cm^{-1}. Meanwhile, the spectrum of $Cu(L\text{-}Leu)_2$ reveals a prominent high-energy shoulder at $\bar{\nu}_4$ since here $\varepsilon_4 < \varepsilon_3$. Shoulders of this type suggest a tetragonal, not a tetrahedronal distortion for equatorial environment [2].

Electronic absorption spectral features as concerns the intensities of peak $\overline{\nu}_2$ and $\overline{\nu}_3$ observed for the Cu(II)-amino acid complexes we have investigated are summarized in Tab.6. By means of this table, it seems feasible to discriminate between fivefold cis and sixfold cis copper complexes. Some workers [17] have recently developed ligand field method to analyze intensity distributions in "d-d" spectra. We believe that, with time, better understanding of the intensities will have been established.

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