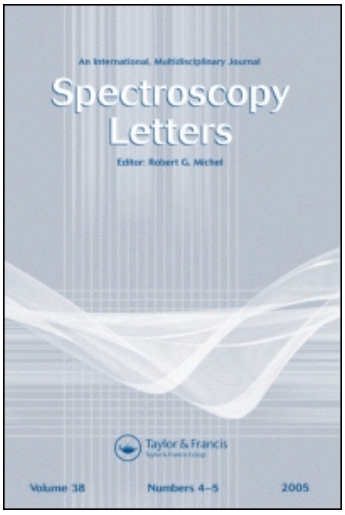

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Spectroscopic and Structural Studies of Complex of Copper (II) with L-Glutamic Acid and 1, 10-Phenanthroline

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SPECTROSCOPIC AND STRUCTURAL STUDIES OF COMPLEX OF COPPER(II) WITH L-GLUTAMIC ACID AND 1,10-PHENANTHROLINE

Key words: electronic absorption spectrum, photocoustic absorption spectrum, aqua(L-glutamato)(1,10-phenanthroline) copper(II) trihydrate, ligand field theory and structural studies

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ABSTRACT

Electronic absorption spectrum and photocoustic absorption spectrum of aqua(L-glutamato)(1,10-phenanthroline)copper(II) trihydrate have been measured. The experimental results are discussed quantitatively with LFT (ligand field theory) and the radial wave function of nonfree copper(II). The features of crystal structure of the title compound are also studied with our theory and the spectra above.

INTRODUCTION

There is great interest in the coordination behavior of glutamic acid to metal ions, from either a biological or a coordinative point of view. Glutamic acid is able to act as bidentate or tridentate ligand.

The crystal structure and spectroscopic properties of aqua(L-glutamato)(1,10-phenanthroline) copper(II) trihydrate (abbreviated [Cu(L-Glu)(o-phen)(H_2O)] · $3H_2O$) have been investigated [1]. Two crystallographically independent [Cu(L-Glu)(o-phen)(H_2O)] discrete molecules were found [1]. They were both distorted square pyramid. In this paper, we report the electronic absorption spectrum and PA (photocoustic absorption) spectrum of the title compound, and interpret them with our theory with relation to the crystal structure. It could be found that our two spectra are more distinct and of greater relevance than the transmission spectra L. Antolini et al. reported [1] in the light of the utility of spectroscopy in elucidating the probable coordination geometries of complexes.

PA spectrum is well-known to be advantageous to the investigation of the spectroscopic properties of general solid. Since, up to the date, there is difficulty in synthesis of crystals for all metal-amino acid complexes, particularly for Fe(II)-amino acid complexes, it is thus of considerable importance to study the PA spectrum of complexes.

EXPERIMENTAL

The title complex was prepared by dissolving Cu(L-Glu) · $2H_2O$, whose preparation has been reported [2], and 1,10-phenanthroline in a 1 : 1 molar ratio, in hot water/methanol (3 : 1). With the solution standing for a few days, blue crystals were separated.

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

Electronic absorption spectrum of the title complex was measured at room-temperature in the region of 4000-30000 cm^{-1}, using the electronic absorption spectrograph, which was made by the institute of Geochemistry, Academia Sinica, for small crystals. The result measured is shown only from 6000-22000 cm^{-1}.

As to the PA spectrometer, excitation source was a 500 W xenon lamp with a CT-30F monochromafer in the region of 300-800nm. The light source intensity was modulated by using a variable speed mechanical chopper at frequency of 12 Hz. The room-temperature PA signal was detected with an

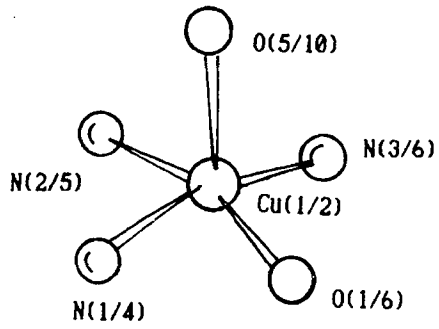

FIG.1. The crystal structure of [Cu(L-Glu)(o-phen)(H_2O)] · $3H_2O$

electret microphone. Output signal was normalized for the changes in lamp intensity by a reference of carbon black. Only the region from 400 to 800nm (25000-12500 cm^{-1}) was drawn for the PA spectrum of the title compound.

RESULTS AND DISCUSSION

The copper coordination as a distorted square pyramid, with the organic ligands acting as bidentate in the equatorial plane and water molecules occupying apical position, is exhibited in Fig.1.

In the crystals of the title compound, ring-stacking interactions between aromatic ligands are found to be major contributors to molecular packing. Further contribution to the crystal-packing forces comes from hydrogen-bonding interactions [1]. Glutamic acid is bidentate ligand for one copper(II), which results in discrete molecules of the title complex, unlike the crystals of (L-glutamato)(imdazole) copper(II), in which L-glutamic acid acts as tridentate ligand, bridges two copper(II), and therefore produces one-dimensional polymeric structure [1].

It should be remarked that two crystallographically independent [Cu (L-Glu)(o-phen)(H_2O)] discrete molecules [1] are present in the crystals of the title complex. They differ from each other in the structural data

TABLE 1.

The data of the crystal structure of the title compound

R, θ, Φ	O(1/6)	O(5/10)	N(1/4)	N(2/5)	N(3/6)
R^a (A·)	1.913	2.294	2.015	2.018	2.020
R^b (A·)	1.926	2.225	1.997	2.027	2.003
θ^a(deg.)	98.3	0	92.5	89.2	94.5
θ^b(deg.)	96.8	0	91.1	89.2	103.9
Φ^a(deg.)	90.2	—	0	277.6	171.9
Φ^b(deg.)	91.4	—	0	277.8	173.5

a: attached to Cu(1)O(1)O(5)N(1)N(2)N(3) chromophore; b: attached to Cu (2)O(6)O(10)N(4)N(5)N(6) chromophore, and hereafter.

(Tab.1). The same case has also been found and proposed to be due to the different arrangements of the hydrogen bonding [3]. We infer that the presence of inequivalent sites may give rise to an overlapping effect on our spectra.

The data of crystal structure are listed for the title compound in Tab.1 in globe coordinate with Cu(1)--O(5) and Cu(2)--O(10) chosen as Z axis. The symmetry of copper coordination is regarded as C_1. According to the environment of Cu(II), Tab.1 and the coordinate system we have taken,the original data can be set up. We here condition our calculation upon strong field and leave out configuration interactions (CI) since the low symmetry may result in considerable d-electronic energy level splits and too weak CI. The parameters of crystal field and electronic energy level of the title compound are calculated with the PLFT [4]. The values are shown in Tab.2 and Tab.3 respectively.

In Tab.2, Ω is defined by Zhang Rongchun and Li Jianmin in their scaling radial wave function theory of nonfree ion [5] as non-freedom, a parameter variable to describe the deviation of central metal ions from free ions. It is given by the expression:

$$\Omega = N\mu/\bar{R}^2 = kN\overline{\mu}/\bar{R}^2(1-t/2)^2$$

TABLE 2.

The crystal field parameters of the title compound

Parameter	Value[a]	Value[b]	Parameter	Value[a]	Value[b]
$\overline{\mu}$ (Debye)	1.15520	1.15520	a_1	0.58527	0.58523
t	0.04670	0.04699	a_2	0.63833	0.63879
Ω(Hartree)	0.16658	0.16639	$\langle r^2 \rangle$ (a.u)	2.02847	2.02688
N	0.9760	0.9600	$\langle r^4 \rangle$ (a.u)	11.23182	11.21184
p^2	1.63631	1.60457	$\langle r^{-3} \rangle$(a.u)	5.74321	5.74512
p^4	2.06175	2.02849	B (cm^{-1})	1016	1016
ζ_1	5.86660	5.86721	C (cm^{-1})	3470	3471
ζ_2	1.85796	1.85871	ζ_{3d}(cm^{-1})	556	557

TABLE 3.

The electronic absorption spectrum of the title compound

Assignment	Cal.[a]	Obs.[a]	Cal.[b]	Obs.[b]
^2A ($^2E_{gb}$,e)	0	0	0	0
^2A ($^2T_{2gc}$,t)	8685	9031	8110	8004
^2A ($^2E_{ga}$,e)	13228	12089	11849	11392
^2A ($^2T_{2ga}$,t)	14391	14200	13494	13100
^2A ($^2T_{2gb}$,t)	16616	17630	15355	15506

where N is the number of ligand ions, $\overline{R}$ is the average bond length, k= 0.393427, t is the ratio of dipole length and bond length, and $\overline{\mu}$ is the dipole moment of the ligand ion (in Debye). Structure I (attached to Cu(1)O(1)O(5)N(1)N(2)N(3) chromophore, hereafter) presents a greater Ω (0.16658) than that (0.16639) of structure II (attached to Cu(2)O(6) O(10)N(4)N(5)N(6) chromophore, hereafter), which indicates the copper (II) ion in structure I is more firmly bound than that in structure II. This conclusion corresponds to the fact that the displacement of the Cu atom toward the apical ligand in structure I (0.123A·) is smaller than

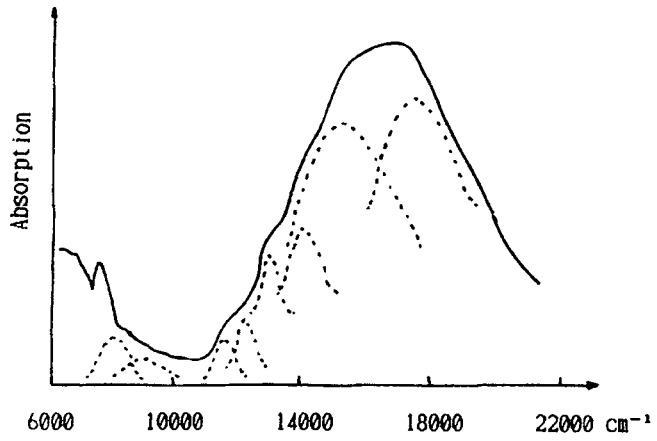

FIG.2 The electronic absorption spectrum of $[Cu(L\text{-}Glu)(o\text{-}phen)(H_2O)] \cdot 3H_2O$

that in structure II (0.186A°) [1]. We think greater displacement of the copper atom toward the apical ligand is due to shorter apical bond length (Tab.1, Fig.1). Thus, greater apical bond length in chromophore should accompany a more firmly bound central ion and lead the d-d bands to blue shifts.

The room-temperature electronic absorption spectrum of the title complex is given in Fig.2. The spectrum apparently consists of multiple bands due to the two different structures in the crystal. After analyzed into Gaussian components on an IBM PC/XT computer with a program of Fan Jifa [6], the spectrum clearly shows two groups of absorption bands, each including four bands. One group (named group I, hereafter) provides absorption bands at about 9031, 12089, 14200 and 17630cm^{-1} respectively, while another group (named group II, hereafter) at about 8004, 11392, 13100 and 15506cm^{-1} respectively. For the reason we have just discussed, group I is assigned to the bands of structure I while group II assigned to the bands of structure II. These experimental results coincide well with our calculation (Tab.3).

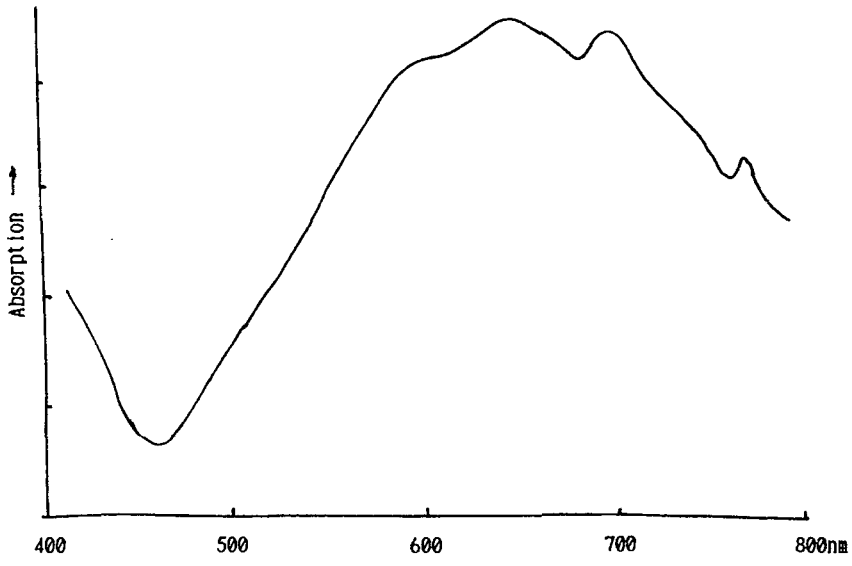

FIG.3. The PA spectrum of $[Cu(L\text{-}Glu)(o\text{-}phen)(H_2O)] \cdot 3H_2O$

The band maxima appearing at the highest energy position in the two groups fall below 18000 cm^{-1}, comparing well those of the CuO_xN_y (x+y=5) complexes we have studied [4].

Although the PA spectrum of the title compound can only give bands in the range of 800-400nm (12500-25000cm^{-1}), it also reveals two groups of bands, one group providing absorption bands at 695nm (14388 cm^{-1}) and 580nm (17241 cm^{-1}) while another group at 763nm (13102 cm^{-1}) and 645 nm (15504 cm^{-1}). They are the high energy parts of group I and II named above respectively. It should be emphasized the bands in the PA spectrum are in accord with those in the electronic absorption spectrum and even more distinct.

It is noteworthy that our spectra readily exhibit two groups of similar absorption bands, suggesting the presence of two ineqivalent sites in the crystal. On the other word, our spectra can be used to tell

one structure from another very similar structure as we have reported in one of our previous communications [7], while the polycrystalline ESR spectrum and transmission spectrum of the title compound reported by L. Antolini et al. can not [1].

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