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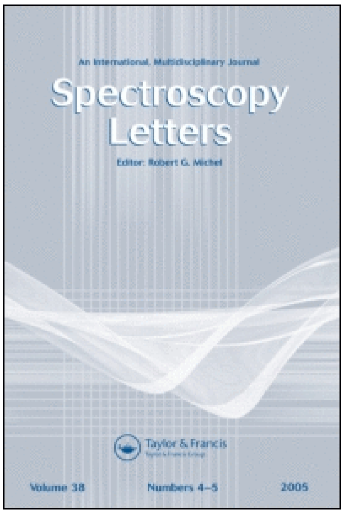

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Spectroscopic and Structural Properties of Dichloro (L-histidine) Copper (II) Crystal

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SPECTROSCOPIC AND STRUCTURAL PROPERTIES OF DICHLORO(L-HISTIDINE) COPPER(II) CRYSTAL

Key words: spectroscopic, dichloro(l-histidine) copper(II)

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ABSTRACT

The electronic absorption spectrum, photoacoustic absorption spectrum (PAS) of dichloro(L-histidine) copper(II) crystals are recorded and discussed quantitatively with ligand field theory (LFT) and the radial wave function of non-free copper(II); our calculation and the two spectra suggest occurrence of significant magnetic exchange interaction.

INTRODUCTION

For the essential significance in biological system and biochemistry, transition metal amino acid complexes have been widely studied. Histidine (HisH), $C_6H_9N_3O_2$, has been shown to be very versatile in the way it can act as a chelating ligand to copper(II), especially for, depending on the PH, histidine can be present either as a neutral molecule or as an anion. The crystal structure of the title compound has been reported.[1] In this paper, electronic absorption spectrum and PAS are determined and explained. The electronic structure of this compound is also

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discussed. Because the distance (nearly 3.6Å) of two copper(II) cations is so short there will exist a strong magnetic exchange interaction between two copper(II) cations and it will be evidently shown in its absorption spectra.[2]

PAS is capable of detecting very weak absorption. The choice of PAS in our recent investigation is made by considering the fact that there appear difficulties in synthesis of crystals for all metal-amino acid complexes while PAS is advantageous to the study of spectroscopic properties of general solid,[3] which may be in amorphous state.

EXPERIMENTAL

For the title complex, blue crystals were obtained from the mixture solution of $CuCl_2$ and L-histidine in the molar ratio 1:1. The crystals give an electronic absorption spectrum consisting of a strong broad band, thus the d-d transition absorption peaks undistinguished. After resolved by an IBM PC/XT programme,[5] the spectrum exhibits four absorption peaks at near 12190,13699,14942 and 16282 cm^{-1}(Fig 1). These values are also listed in Tab. 1 as observed ones.

DISCUSSION

It can be appreciated in Fig.2 that the room-temperature PAS presents a band centred at 675 nm(14800 cm^{-1}). The band is considered to correspond to the combination of peak γ_3 in the electronic aborption spectrum. In the corresponding region (500-800 nm), PAS is thereby apparently coincident with the d-d transition spectrum. It should be emphasized that the PAS of the title compound additionally reveals a shoulder at 340 nm while shoulders of this sort have not been found for bis(L-histidine) copped(II) dinitrate dihydrate. In consideration of their crystal structures,[1,6] we are forced to the conclusion that the shoulder appearing at 330 nm arises from the $\Pi(Cl)\Rightarrow Cu(II)$ LMCT of Cu-Cl-Cu bridges .

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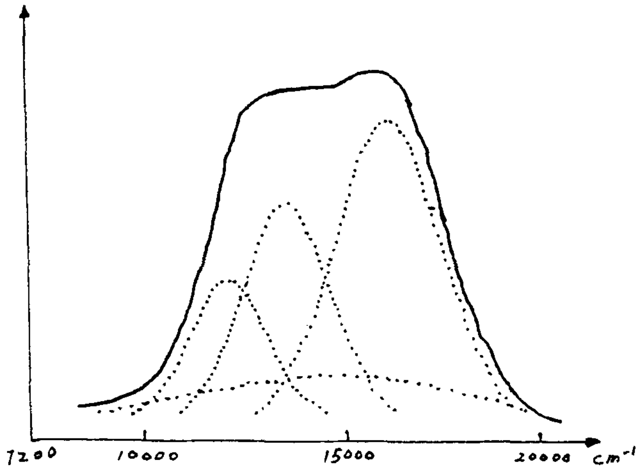

FIG 1. The electronic absorption spectrum of Cu(L-HisH)Cl$_2$

TABLE 1 The d-d Transition Energy of Cu(L-HisH)Cl$_2$ (unit:cm^{-1})

Peak	Obs.	Calc.		
		square	square-pyramid	octahedron
γ_1	12190	8417	11715	18643
γ_2	13699	15405	14854	22267
γ_3	14942	15597	17310	26322
γ_4	16282	16015	17898	27179

Where the four peaks are rowed up as γ_1, γ_2, γ_3, and γ_4 by the order of low to high energy.

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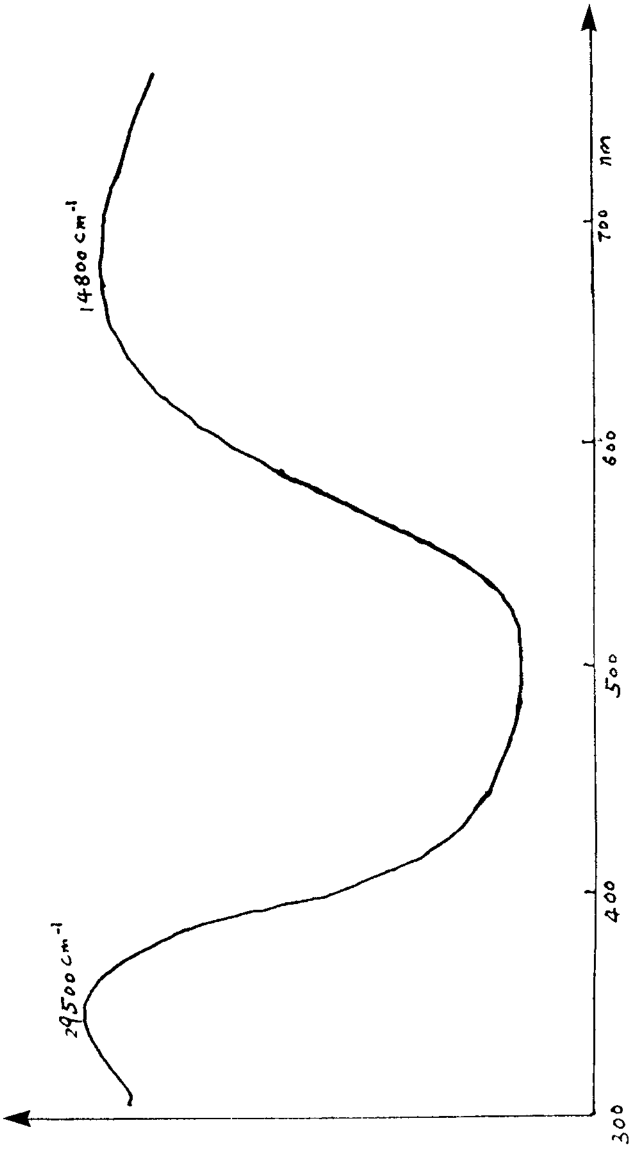

FIG 2. The photoacoustic absorption spectrum of Cu(L-HisH)Cl2

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The crystal structure[1] of the title complex consists of chains of molecules with the carboxy oxygen atom, the amine nitrogen atom and the two chlorine atoms forming as approximate square-plane about the copper atom with two bridging chlorine atoms from two adjacent molecules completing a distorted octahedron. The coordination structure is shown in Fig.3 with its data collected in Tab. 2 in globe coordinate.

In ligand field theory. Li Jianmin had suggested a non-free ions wave function radial scaling theory for which a program package(PLFT) had been developed and the radial wave function of Cu(II) can be written in double ζ as [7,8]

$$R_{3d}(r,\Omega)=C^{-1/2}[0.55428\ STO(\zeta_1) + 0.60500\ STO(\zeta_2)]$$
$$=a_1STO(\zeta_1)+a_2STO(\zeta_2)$$

where,

$\zeta_1= 6.3496\ (1-0.41500\ \Omega +0.25000\ \Omega^2)$,

$\zeta_2= 2.5250\ (1-1.64500\ \Omega +0.35500\ \Omega^2)$,

C is normalization coefficient, and Ω is so-called scale of nonfreedom, a variable parameter determined by the number of ligands, average bond length, the ratio of dipole length and bond length (t), and the average dipole moments of ligands ($\bar{\mu}$), to describe the deviation of central ion from free ion.

With this theory, the electronic structures of hundreds of complexes have been explained perfectly.[9] For the title compound the symmetry is regarded as C_1. The out-of-plane Cu--Cl bonding interactions, Cu--Cl(6) bonding interaction in particular, were thought very weak because of the long bonds of 2.941 and 3.138 Å (The sum of Van der Waals radii is 3.1-3.3Å).[1] We therefore condition our calculation upon four, five and six-coordination respectively. According to the environments of Cu(II),Tab. 2 and the coordinate system we have taken, original data can be set up. The crystal field parameters and d-d transition energies are

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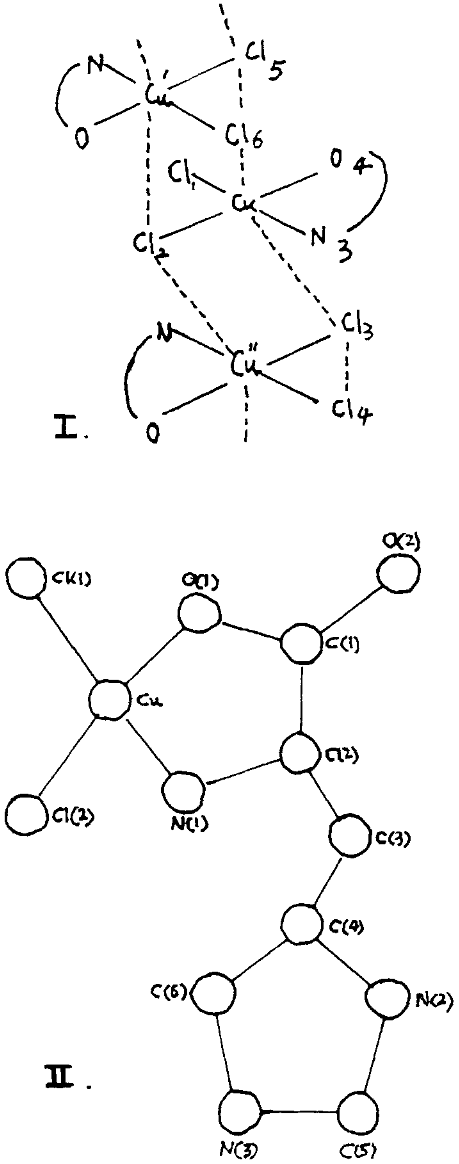

FIG 3. The coordination structure of Cu(L-HisH)Cl2

TABLE 2 The Coordination Structure Data of Cu(L-HisH)Cl_2

No.	O(1)	Cl(2)	Cl(3)	N(4)	Cl(5)	Cl(6)
R(Å)	1.980	2.254	2.293	1.980	2.941	3.138
θ(deg.)	90.0	90.0	90.8	89.5	30.0	180.0
Φ(deg.)	0	94.4	187.2	275.4	330.0	--

TABLE 3

Crystal Field Parameters of Cu(L-His)Cl_2(assumed Square-pyramidal)

parameter	value	parameter	value
μ(Debye)	1.62040	a1	0.59816
t	0.03073	a2	0.65290
Ω(Hartree)	0.22815	$\langle r^2 \rangle$(a.u.)	2.64636
$\bar{N}$	0.9000	$\langle r^4 \rangle$(a.u.)	19.79845
$p^{(2)}$	1.59267	$\langle r^{-3} \rangle$(a.u.)	5.15721
$p^{(4)}$	2.00578	B(cm^{-1})	900
ζ_1	5.66578	C(cm^{-1})	3091
ζ_2	1.62401	ζ (cm^{-1})	488

where B and C are Racah's parameters, ζ_{3d} represents spin-orbital coupling constant, and $p^{(2)}$ and $p^{(4)}$ are polarization factors defined by us.

calculated using PLFT. The results are listed in Tab.1 and Tab. 3 as calculated values. It is found from Tab. 1 that the values calculated for square-pyramidal copper(II) are something in accord with the experimental ones, though values obtained from these three coordination structures are all unsatisfactory (Herein, the errors of the positions of absorption peaks are much more larger than the usual value 5%). The large errors probably result from the structure of Cu-Cl-Cu bridges.

The room-temperature powder ESR spectrum is characterized by both $g_{//}$(2.181) and $g_{\perp}$(2.078) values greater than 2.040, conforming to a ground state configuration with the unpaired electron in the

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dx^2-y^2 orbital[10]. The ESR spectrum gives little information about the magnetic exchange interaction of the title compound while our electronic absorption spectrum and PAS have indicated this significant interaction which was ever predicted by K.Colyvas and co-workers.[1]

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