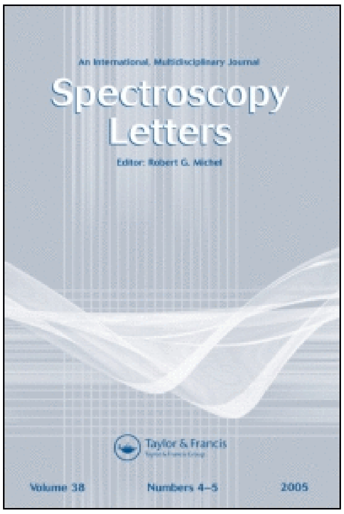

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Photoacoustic Spectroscopical Studies on [Cu(Cl)(Gly)(O-Phen)]·H_2O Crystal

Li jianmin[a]; Wang jinbu[a]; Xu min[a]; Zhang yugen[a]
[a] Department of Chemical Physics, University of Sci. and Tech. of China, Hefei, Anhui, P.R.China

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PHOTOACOUSTIC SPECTROSCOPICAL STUDIES ON $[Cu(Cl)(Gly)(O\text{-}phen)]\cdot H_2O$ Crystal

Key words: Glycinato, PLFT, Photoacoustic spectrum, $[Cu(Cl)(Gly)(O\text{-}phen)]\cdot H_2O$

Li jianmin, Wang jinbu, Xu min, Zhang yugen

Email: jmli@dchp.chp.ustc.edu.cn
Department of Chemical Physics,
University of Sci. and Tech. of China,
Hefei, Anhui, 230026, P.R.China

ABSTRACT

The amino-acid copper crystal of $[Cu(Cl)(Gly)(O\text{-}phen)]\cdot H_2O(I)$ was synthesized and its photoacoustic spectrum was recorded under normal atmosphere temperature . A semi-empirical method of coordinate-field-theory PLFT was utilized to calculate the d-d transition energy. According to the results, the spectrum was explained satisfactorily.

INTRODUCTION:

Metal proteins have great significance in life activities. Many metal proteins act as high selective and efficient catalysts in biological process in living bodies[1].

The Glycine is one of the necessary amino acid in human body. Interest in mixed ligand chelate complex has been clearly established in the last few years[2].

In recent years, the spectra of many types of solid, crystals, powder or gel, have been recorded by photoacoustic measurement. So photoacoustic spectrum has been widely used to investigate the chemical and physical properties of almost all kinds of samples. If the sample is not luminescent, the photoacoustic spectrum will coincide with the electronic absorption spectrum.

EXPERIMENT :

The dark blue object complex was prepared by a method submitted by Ref.[3]. The photoacoustic spectrum was recorded between 300 nm and 800 nm region under room temperature. The excitation source was a 500W Xenon lamp, and the light source was modulated by a variable speed mechanical chopper at a frequency of 12HZ. The sample was placed in a locally built photoacoustic cell fitted with an ERM10 electret microphone ,and the acoustic signal was detected. Finally, the output signal was normalized for changes in lamp intensity using a carbon-blank reference.

RESULTS AND DISCUSSIONS:

1. Description of the object crystal structure

The space coordinate condition of [Cu(Cl)(Gly)(O-phen)]$\cdot H_2O$(I) is shown in **FIG.** 1 [1]. The Cu atom displays a distorted squarepyramidal coordination, with the phenanthroline and amino-acid ligands in the basal plane and a Cl atom in the apical site. The average Cu-O And Cu-N(amino acid) bond lengths are 1.936(6) and 2.006(8)Å[3]. To make it convenient in theoretical calculation, the structure was described in a pole coordinate system. The values are given in Table1.

2. Theoretical calculation and spectrum resolution

The photoacoustic spectrum of the title complex is given in Figure 2. According to the figure , A broad intense peak in 15900 cm^{-1} and a relatively sharp peak in 27730 cm^{-1} were

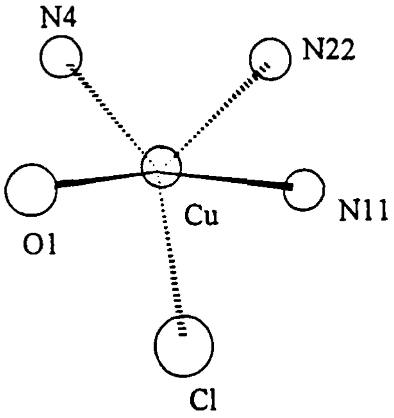

FIG. 1 Coordinate structures of the crystals $[Cu(Cl)(Gly)(O\text{-}phen)]\cdot H_2O$(**I**)

Table 1: The data of The object complex structure of $[Cu(Cl)(Gly)(O\text{-}phen)].H_2O$(I)

R, θ ,ϕ	O(1)	N(4)	N(22)	N(11)	Cl
R(Å)	1.945	2.007	2.031	2.007	2.546
θ(deg.)	100.9	103.4	93.5	100.6	0
ϕ(deg.)	191.2	262.1	0	81.6	—

displayed. Compared with the photoacoustic spectrum of $[Cu(L\text{-}phe)(O\text{-}phen)\ (H_2O)]\ NO_3H_2O$ (II)[5], 16050 cm^{-1} and 30300 cm^{-1}, both the peaks of the complex (I) have red shifts, 150 cm^{-1} and 2570 cm^{-1}.

First, the relatively sharp peak of the photoacoustic spectrum of (**I**) in near ultraviolet region suggests that it is not a ultraviolet absorption of the Π orbital absorption of the ligands , and it is can be attributed to the LMCT transition from

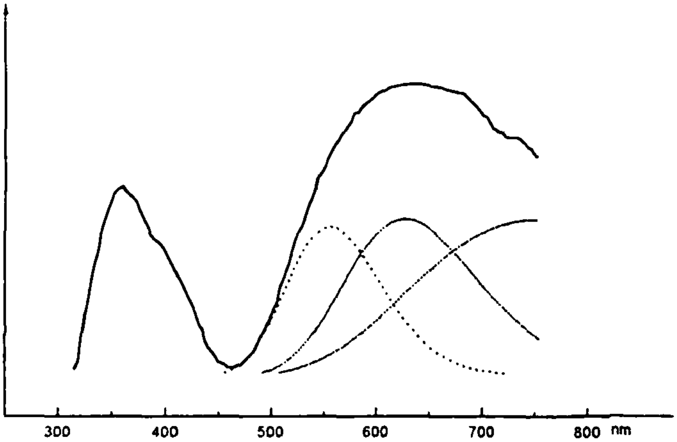

FIG 2:. Photoacoustic spectra of the title complex(I)

the Π orbitals of the ligands to the d orbitals of central metal ion Cu(II) [6]. The broad intense peak in 15900 cm^{-1} is assigned to the d orbitals electronic transition of the central ion Cu(II) . The spectrum is not sharp peaks caused by split d-d energy gap, which is resulted from the following reasons: **1**. Crystal grating vibration. **2**. Jahn-Teller effect. **3**. The low symmetry of the coordinate field. So a semi-empirical method PLFT[7-11] of the coordinate field theory was utilized to resolve the d energy level.

In ligand field theory, Li jianmin et al.[6] had suggested a non-free ion wave function radial theory and developed a program package(PLFT) for calculation of this ligand field theory, which is such a software pack: Point electric charge-electric dipole model is adopted; Under central-force field approximation, radial wave functions of non-freedom transition-metal ions are determined. With strong-field disposal of the coordinate theory, the software was made in FORTRAN77 . In this software pack, the only one adaptable parameter is convalency factor $\tilde{N}$, which is between 0.8 and 1.0. So far, spectrum properties of more than one hundred transitional-metal complexes were successfully explained by this software pack[4]. According the theory the radial wave function of non-free Cu(II) can be written in double ζ as [6]

$$R3d(r,\Omega)=C\text{-}1/2[0.55428STO(\zeta_1)+0.60500(\zeta_2)]$$

$$=a1STO(\zeta_1)+a2STO(\zeta_2)$$

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

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

$$C=1-0.67078\{0.48719-[2(\zeta_1\zeta_2)^{1/2}/(\zeta_1+\zeta_2)]^7\}$$

Where C is normalization coefficient, and Ω so-called scale of non-freedom, a variable parameter used to describe the deviation of the central ion from free ion. It is given by the following equation:

$$\Omega=N\mu/R\mu^2=KN\mu/[R^2(1-t/2)^2]$$

Where N is the number of ligand ions, R is average bond length, t is the ratio of dipole length to bond length, and μ is dipole moment of ligand ion(in Debye). From the crystal structure data listed in Table **1** and using the PLFT, the parameters of the crystal field are listed in the following Table **2**, the values of calculated electronic energy are listed in the following Table **3**. It is concluded from the values of calculated electronic energy in Table **3** that the intensity and position of the broad peaks of the crystal (**I**) are generally determined by ν_3 , which was agreed with the our results: The position of the broad peak 15900 cm^{-1} is just around ν_3. So the photoacoustic spectrum is satisfactorily explained. The red shifts of the two peaks in the object crystals (**I**) and (**II**) photoacoustic spectra are resulted from the difference of their structures. The amino acids of (**I**) and (**II**) are different, but their coordinate environments are same with each other, CuN_3O_2. However, their

Table 2: The crystal parameters of $[Cu(Cl)(Gly)(O\text{-}phen)]\cdot H_2O(I)$

μ	1.33720	a1	0.59141
t	0.04839	a2	0.64553
Ω	0.19634	$\langle R^2 \rangle$	2.29660
$\tilde{N}$	0.9480	$\langle R^4 \rangle$	14.65619
P2	1.62501	$\langle R^{-3} \rangle$	5.45521
P4	2.07985	B	959.
ξ_1	5.77105	C	3283.
ξ_2	1.74405	ξ_{3d}	523.

Table 3: Values of d-d transition energy of $[Cu(Cl)(Gly)(O\text{-}phen)]\cdot H_2O(I)$ (cm^{-1})

Peak	transition ($\rightarrow dx^2\text{-}y^2$)	calc.
ν_1	dxy	7765
ν_2	dyz	13267
ν_3	dxz	15991
ν_4	dz^2	17840

conformation is different. Referring to the crystal $[Cu(Cl)(Gly)(O\text{-}phen)]\cdot H_2O$(I), the loss of planarity of the Cu atom is larger than that of the Cu atom in the complex $[Cu(L\text{-}phe)(O\text{-}phen)(H_2O)]NO_3H_2O$(II) [5]. The square-pyramidal of (I) distorted toward a trigonal-bipyramidal geometry, and the Cu-O and Cu-N(amino acid or phenanthroline) bond lengths of (I) is longer those of (II), displayed in Table. So the broad peak in photoacoustic spectrum will red shift and its intensity will increase. Ref.[12], which is in agreement with d-d spectrum [12].

From the analysis above, the spectroscopic properties, electronic structure and crystal structure are agreed with each other. The red shifts of two peaks suggest that the change of photoacoustic spectrum is attributed to the difference of crystal geometry, and is consistent with the geometry.

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