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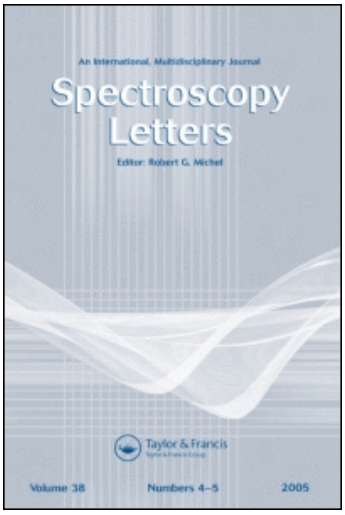

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Studies on the Electronic Absorption Spectrum and Photoacoustic Spectrum of $[Cu(L\text{-}ArgH)_2(Ac)_2]\ 3H_2O$ Crystal.

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Studies on the Electronic Absorption Spectrum and Photoacoustic Spectrum of $[Cu(L-ArgH)_2(Ac)_2]$ $3H_2O$ Crystal.

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KEY WORDS:

Photoacoustic spectrum,Electronic absorption spectrum

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ABSTRACT:

The crystal of $[Cu(L-ArgH)_2(Ac)_2]3H_2O$ was synthesized and its electronic absorption spectrum and photoacoustic spectrum were recorded under room temperature. The spectrums were compared with each other.A semi-empirical method of coordinate-field-theory PLFT was utilized to calculate the transition energy.With the results, we satisfactorily resolved the spectrums, and the resolution was discussed.

INTRODUCTION:

Metal proteins play a very important role in life activities. Firstly,metal proteins are high-efficient,high-selective catalysts acting as proteinases during the biological processes in the

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bodies.Secondly,metal proteins are of great significance in the respiration processes as oxygen supports such as ferrohemoglobin and cuprein.Considerating that the proteins are composed of amino -acid units,chemists have carried out a great deal of researches on the coordinate complexes of the amino-acid ligands with the transition-metal central ions[1].

The electronic absorption spectrum is of great importance in studying the molecular structure of coordinate complexes, and in recent years photoacoustic measurements have been widely used to investigate the chemical and physical properties of almost all kinds of samples, the precedence is that it enables the scientists to obtain spectrums of any type of solid[2], whether it is crystalline,powder or gel. Theoretically, if the sample is not luminescent, the electronic absorption spectrum will coincide with the photoacoustic spectrum in expressing d-d electron transition.

This paper is one part of series of our work, some of which have already been published[3][4][5].

EXPERIMENTAL:

Single crystals of the compound were obtained from cold ethanol-water mixtures containing 1 mmol of copper acetate (0.1997g) and 2mmol of L-argimine(0.3484g). In a typical preparation,the copper acetate was dissolved in the minimum amount of water and a solution of the amino acid(20ml) added.Blue crystal separated after two or three weeks[6]. Elemental analyses were measured using a Perking-Elemer 240C and the results were: Exp: C:32.67, H:6.98, N:19.34. Cal: C:32.78, H:7.14, N:19.12.

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We recorded the electronic absorption spectrum and the photoacoustic spectrum of the sample under room temperature. Electronic spectrum was recorded in the region from 6000 to 24000cm^{-1}. The photoacoustic spectrum was recorded in the region from 300-800nm. The excitation source was a 500W xenon lamp.The light source was modulated by a variable speed mechanical chopper at a frequency of 12Hz. The acoustic signal was detected with the sample placed in a locally built photoacoustic cell fitted with an ERM 10 electret microphone. The output signal was normalized for changes in lamp intensity using a carbon-blank reference.

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RESULTS AND DISCUSSION:

1.Description of the molecular structure

The crystal of $[Cu(L-ArgH)_2(Ac)_2]3H_2O$ contains two differently structured formula units. The two formula units form a dimer and they are connected with each other and to those in other dimers via a complex series of electrostatic interactions and hydrogen bonds, the axes angle of the two formula units is 180°.The complex has a very low symmetry, its approximate point group is C_1. To make it more convenient in theoretical calculation,we describe the structure in a pole coordinate system(Figure1), the values are given in Table1.

2.Theoretical calculation and the resolution of the spectrum

The electronic absorption spectrum and photoacoustic spectrum which we obtained in the experiment are given in Figure 2-3. A broad and strongly-absorbed peak at 17200cm^{-1} is shown in the

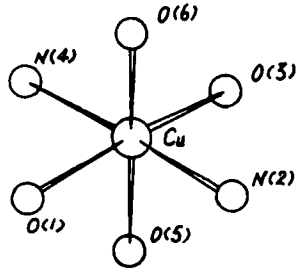

Figure 1.

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electronic absorption spectrum and the photoacoustic spectrum has a similar peak at 16920cm^{-1}. We can see that the electronic absorption spectrum and the photoacoustic spectrum coincide with each other in expressing the d-d electron transition.Successful resolution of one spectrum is also the explanation of the other spectrum.It confirms our earlier anticipation: Under the condition that the sample is not photoluminescent, the electronic absorption spectrum coicide with the photoacoustic spectrum[7].

The electronic absorption spectrum of $[Cu(L-ArgH)_2(Ac)_2]3H_2O$ displays a strongly-absorbed broad peak, not sharp peaks caused by split d-d energy gap as we anticipated. It is caused by the following reasons:1.Crystal grating vibrations.The vibrations make the distances between central ions and the coordinate atoms change quickly in a certain region, which makes the coordinate field intensity fluctuates in a certain region. 2. Janh-Teller effect.3.

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TABLE1

The data of the crystal structure of $[Cu(L\text{-}ArgH)_2(Ac)_2]3H_2O$

	R,Θ,ø	O(1)	N(2)	O(3)	N(4)	O(5)	N(6)
Cu(1)	R(A)	1.936	1.996	1.938	1.991	2.570	2.884
	Θ(deg.)	87.4	91.0	94.2	95.2	0	176.7
	ø(deg.)	0	98.5	181.8	275.9	/	126.4
Cu(2)	R(A)	1.941	1.995	1.944	1.986	2.563	2.944
	Θ (deg.)	85.0	86.9	97.7	94.4	0	177.3
	ø (deg.)	0	94.6	181.6	275.6	/	126.5

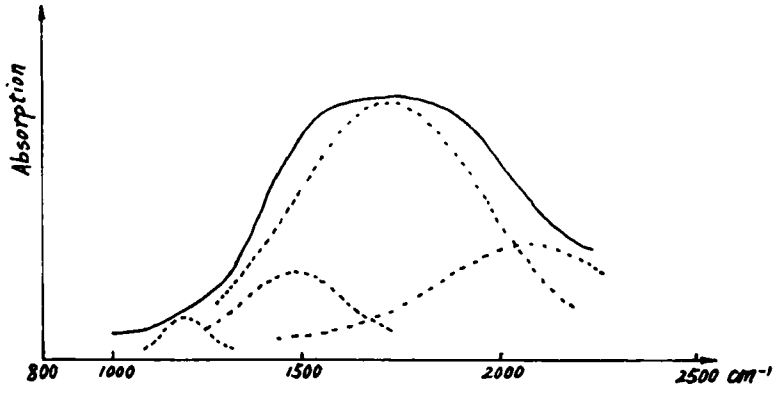

Figure 2.

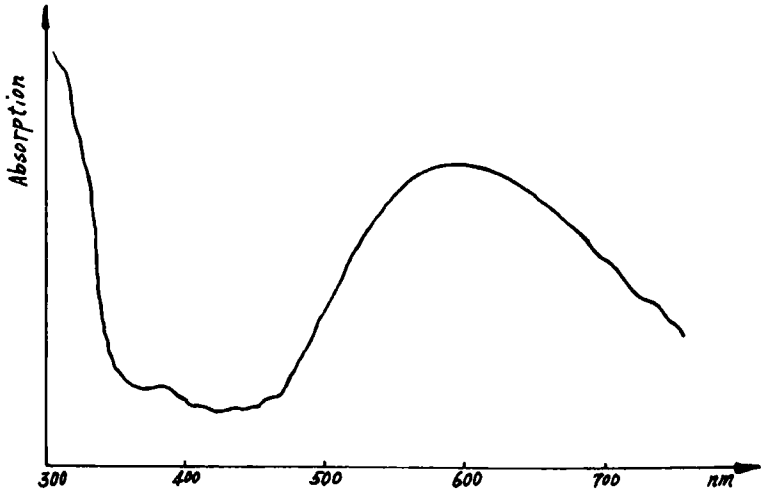

Figure 3.

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The low symmetry of the coordinate field makes the d energy level split. It is necessary to resolve the spectrums in details. We now utilize a semi-empirical method of coordinate-field-theory PLFT which was submitted by Li Jianmin et[8][9][10].

PLFT is such a software pack: Point electric charge-electric dipole model are adopted; Under central-force approximation,radial wave functions of non-freedom transition-metal ions are determined; With strong-field disposal of coordinate-field theory, FORTRON 77 structrural language is utilized to write the software. In this program there is only one adaptable parameter- the convalency factor $\bar{N}^2$, which is between 0.8 to 1.0. So far the program has successfully explained spectrum properties of more than one hundred transition-metal complex crystals.

The parameters of the crystal field and electronic energy level are calculated. The values are shown in Table2. The observed values in Table2 are a issue of computer resolutions.

Theoretical values coincide well with the experimental values,the errors are no more than 10% .Spectrum properties of the sample are well explained.

In the resolved electronic absorption spectrum, we can see $\varepsilon_3>\varepsilon_4>\varepsilon_2>\varepsilon_1$ (absorption intensity). Compared with electronic absorption spectrums of other complex crystal of amino-acid ligands with central ion Cu in Ref[4], the position and the intensity of the broad peak are generally determined by ν_3 and ν_4 transitions.Ref[11] assummed transitions ν_1 and ν_2 are controled

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TABLE2

The d-d transition energy of $[Cu(ArgH)_2(Ac)_2]3H_2O$

Peak	Cal(cm^{-1})	Obs(cm^{-1})
ν_1	12284	12100
ν_2	15438	14538
ν_3	18015	17216
ν_4	19488	20532

by a certain inhibitted transition, so far the assumption has not been proved theoretically.In fact,the intensity distribution of the d-d electronic transition has not been explained by a successful theory yet.

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