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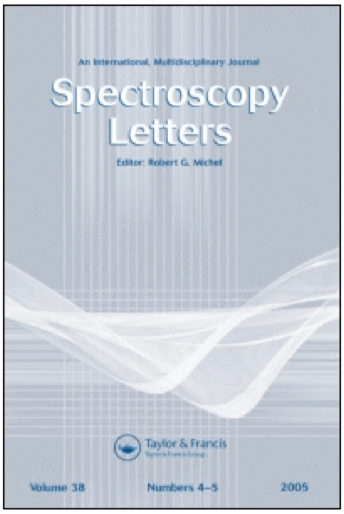

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Spectroscopic Properties and Electronic Structure of (L-Glutamato)(2, 2'-Bipyridine) copper(II)

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SPECTROSCOPIC PROPERTIES AND ELECTRONIC STRUCTURE OF (L-GLUTAMATO)(2,2'-BIPYRIDINE)COPPER(II)

Key words: electronic absorption spectrum,PA spectrum,Cu(L-glu)(bpy) electronic structure,LFT

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ABSTRACT

Cu(L-glu)(bpy)(L-glu=L-glutamato;bpy=2,2'-bipyridine) was prepared.Its electronic absorption spectrum and photoacoustic spectrum were recorded at room temperature.They were compared with each other and compared quantitatively with ligand field theory(LFT) and the radical wave function of non-free ions[1-3].Therefore,the electronic structure was also investigated with its spectrum behaviors and PLFT[1-3].

INTRODUCTION

There are great interests in the coordination ability of amino-acid to metal ions from either a biological or sample coordinative point of view. Metal-glutamate complexes and its adducts with amine have been extensively investigated in solution.It is generally accepted that mononuclear complexes with tridentate glutamate have never been well established[4,5].In fact,in solid complexes glutamate has invariably been found to act as a ligand bri–

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dging,in an extended-chain configuration,two or three metal ions,giving rise to polymeric compounds[4,5,6].

In order to rationalize the condition that may favor polynuclear glutamate species,in this peper we report the spectroscopic and electronic structure investigations on polymeric (L-glutamato)(2,2'-bipyridine)copper(II).

In finding the electronic structure,as we know,the electronic absorption spectrum is more exact than reflecting spectrum.

PAS is well-known to be advantageous to the investigation of the spectroscopic properties of general solid.Since up to data, there is difficult 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 spectra of complexes[7,8].But the photoacoustic spectrum of the title complex has not been found.However,the PA spectra of other complexes system are also very limited[9,10].

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EXPERIMENTAL SECTION

1:Preparation

We prepared the compound of (L-glutamato)(2,2'-bipyridine)copper(II) by dissolving Cu(L-glu)·$2H_2O$,prepared as reported in the ref.[11],and the amine in a 1:1 or 1:1.5 molar ratio,in hot water or water/methanol (3:1) (70°C). When the solution was allowed to stand for some days,deep blue crystals precipitated.According to the ref.[5] and the infrared spectrum of the crystals,we confirmed that it is Cu(L-glu)(bpy).

2:The d-d spectrum and PAS

The electronic absorption spectrum was measured at room temperature in the region of 350-850nm(28600-11760cm^{-1}),using the electronic absorption spectrograph of Sichuan Normal University.Here only the region of 425-700nm was drawn for the d-d spectrum,the result was shown in fig.1.

As to the PA spectrometer, excitation source was 500w Xenon lamp with a CT-30T monochromafer in the region of 300-800nm.Light source intensity was

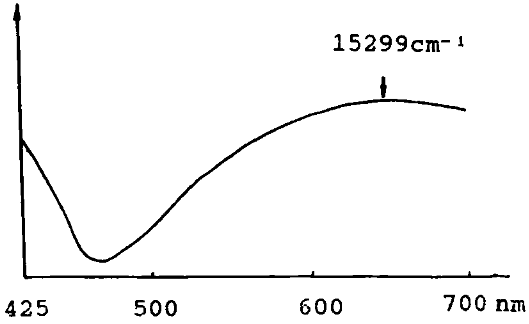

fig.1 The d-d spectrum of Cu(L-glu)(bpy)

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modulated by using a variable speed mechanical chopper at frequency of 12 Hz.The room temperature PA signal was detected with a electrel microphone. Output signal was normalized for the changes in lamp intensity by a referancy of carbon black.See fig.2.

RESULTS AND DISCUSSION

1:Structure description of Cu(L-glu)(bpy)

The structure is built up of two crystallographically independent one-dimensional polymeric chains,whose repetitive units are shown in ref.[5] Each Cu atom exhibits distorted square-pyramidal five-coordination,with the 2,2'-bipyridine molecule and the $L-glu^{2-}$ ion acting as bidentate ligands in the equatorial plane and a γ-carboxylate O atom from a second glutamate ion in the apical position[5].See fig.3.There are two kinds of copper ion which are in different environment in a crystal.Their data of structure are shown in the table 1.The symmetry of Cu coordination is regarded as C_1.

2:Theoretical calculation and the resolution of the spectrum

In accordance with the environment of Cu(L-glu)(bpy), Table 1. Original data can be set up.The parameters of crystal field and the energy level of

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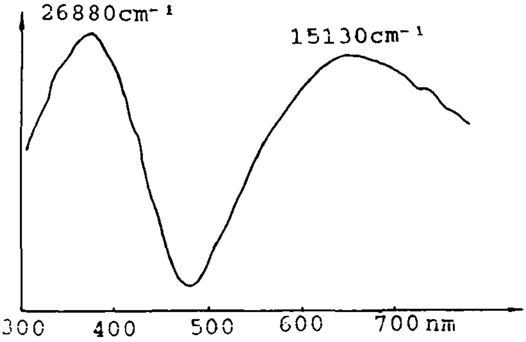

fig.2 The photoacoustic spectrum of Cu(L-glu)(bpy)

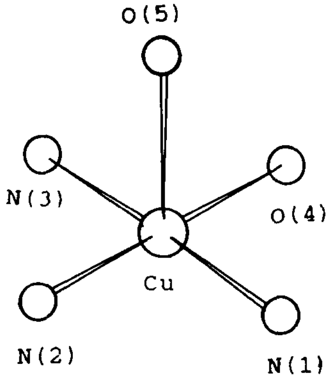

fig.3 The structure of Cu(L-glu)(bpy)

Tab.1: The structural data of Cu(L-glu)(bpy)

		N1	N2	N3	O4	O5
Cu1	R(A)	2.015	1.913	2.020	2.018	2.294
	θ(deg.)	92.5	98.3	94.5	89.2	0
	ϕ(deg.)	0	90.2	171.9	277.6	/
Cu2	R(A)	1.997	1.926	2.003	2.027	2.225
	θ(deg.)	91.1	96.8	103.9	89.2	0
	ϕ(deg.)	0	91.4	173.5	277.8	/

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Tab.2: The structure and spectroscopic properties of Cu(L-glu)(bpy)

structure	coordinate environment	transition ($\rightarrow d_{x^2-y^2}$)	calc. (cm^{-1})	PAS (cm^{-1})	EAS (cm^{-1})
Ref.[5] Fig.3	Cu1: CuN_3O_2	d_{xy} d_{z^2} d_{xz} d_{yz}	9306 11312 13690 14562	15130br 26880 Fig.2	15299br Fig.1
	Cu2: CuN_3O_2	d_{xy} d_{z^2} d_{yz} d_{xz}	10096 10994 14613 14994		

the title complex were calculated with PLFT[1-3].The values were given in the table 2.

The electronic absorption spectrum and PAS of Cu(L-glu)(bpy) showed almost the same absorption position and intensity in their common wavelength region. Peaks lying at 15299cm^{-1} in the d-d absorption spectrum,which is nearly in agreement with 15130cm^{-1} in PAS.They may due to the d-d transition absorption of Cu(II) ion and can be assigned as the transition Cu1:$d_{x^2-y^2}$-d_{yz};Cu2: $d_{x^2-y^2}$-d_{yz},$d_{x^2-y^2}$-d_{xz}.Therefore,according to Tab.2,they can't be shown respectively and only appeared a overlaped broad band.In addition,the broad band probably also imply that the high energy level(being relative to base state) is sensitive to the bond length between ligand and Cu(II),namely coordinate atoms' vibration affects remarkly the high energy level and Jahn-Teller effect. 26880cm^{-1} in PAS may be the metal to ligand charge-transfer (MLCT) spectrum and can be assigned as "Cu(II)-π*(bpy)[12]".

As to the transition peaks which were less than 11400cm^{-1}(see table 2) had not been shown in the d-d spectrum because they have been out of the region that spectrograph can record.Therefore,the d-d spectrum of 425-700nm only had a absorption peak.The absorption peaks which wavelength were more than 700nm in PAS can't be measured as well.

From the analysis above,we found that the spectroscopic properties,electronic structure and crystal structure of Cu(L-glu)(bpy) are agreement with one another.

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