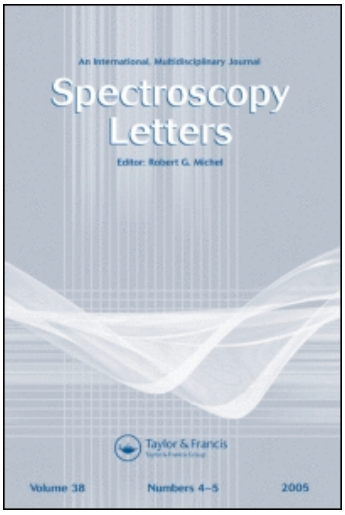

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

SPECTROSCOPIC PROPERTIES AND ELECTRONIC STRUCTURE OF [CuCl(L-PROLINATO)(H_2O)]

Li Jianmin[a]; He Gaofei[a]; Wang Jinbu[a]; Ke Yanxiong[a]
[a] Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, P.R. China

Online publication date: 26 June 2002

To cite this Article Jianmin, Li , Gaofei, He , Jinbu, Wang and Yanxiong, Ke(2002) 'SPECTROSCOPIC PROPERTIES AND ELECTRONIC STRUCTURE OF [CuCl(L-PROLINATO)(H_2O)]', Spectroscopy Letters, 35: 1, 145 — 152
To link to this Article: DOI: 10.1081/SL-120013141
URL: http://dx.doi.org/10.1081/SL-120013141

SPECTROSCOPY LETTERS, 35(1), 145–152 (2002)

SPECTROSCOPIC PROPERTIES AND ELECTRONIC STRUCTURE OF [CuCl(L-PROLINATO)(H_2O)]

Li Jianmin,* He Gaofei, Wang Jinbu, and Ke Yanxiong

Department of Chemical Physics, University of Science and Technology of China Hefei, Anhui, 230026, P.R. China

ABSTRACT

[CuCl(L-Prolinato)(H_2O)] was prepared. Its electronic absorption spectrum and photoacoustic spectrum were recorded at the room temperature. A semi-empirical method of ligand-field-theory PLFT was utilized to calculate the *d-d* transition energy. According to the results, the spectrum was explained satisfactorily.

Key Words: Electronic absorption spectrum; PA spectrum; [CuCl(L-Prolinato)(H_2O)] electronic structure; PLFT

*Corresponding author. E-mail: jmli@ustc.edu.cn

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 Prolinato is one of the necessary amino acid in human body. 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- Prolinato complexes have been extensively investigated in solution.

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

In recently 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. PA spectrum is chosen in our previous work[2,3] because it is advantageous to the investigation of the electronic structure for the complex in general solid state, and up to the date there are difficulties in synthesis of crystals for all metal-amino acid complex.

Herein we reported the spectroscopic and electronic structure investigations of [CuCl(L-Prolinato)(H_2O)].

EXPERIMENTAL

The title complex was prepared as reported[4]. To an aqueous solution (40 cm^3) of copper (II) chloride (1.34 g, 0.01 mol) was added L-proline (1.15 g, 0.01 mol). Blue crystals were obtained form the solution by keeping it in a desiccator containing acetone for one week.

The electronic absorption spectrum (diffuse reflection spectrum) of the title complex was recorded at room temperature in the region of 200–2500 nm, using (HITANCHI) V-34100 UV/VIS, which was made by ANHUI INSTITUTE OF OPTICS AND FINE MECHANICS CHINESE ACADEMY OF SCIENCE. Here only the region of 5000–22,000 $cm^{-1}$was drawn for the *d-d* spectrum, the result was shown in Fig. 1.

The photoacoustic spectrum was recorded between 300 nm and 800 nm region under room temperature. The excitation source was a 500 W Xenon lamp with a CT-30T monochromafer in the region of 300–800 nm. The light source was modulated by a variable speed mechanical chopper at a frequency of 12 Hz. The sample was placed in a locally built photoacoustic cell fitted with an ERM10 electronic microphone, and the acoustic signal was detected. Finally, the output signal was normalized for changes

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

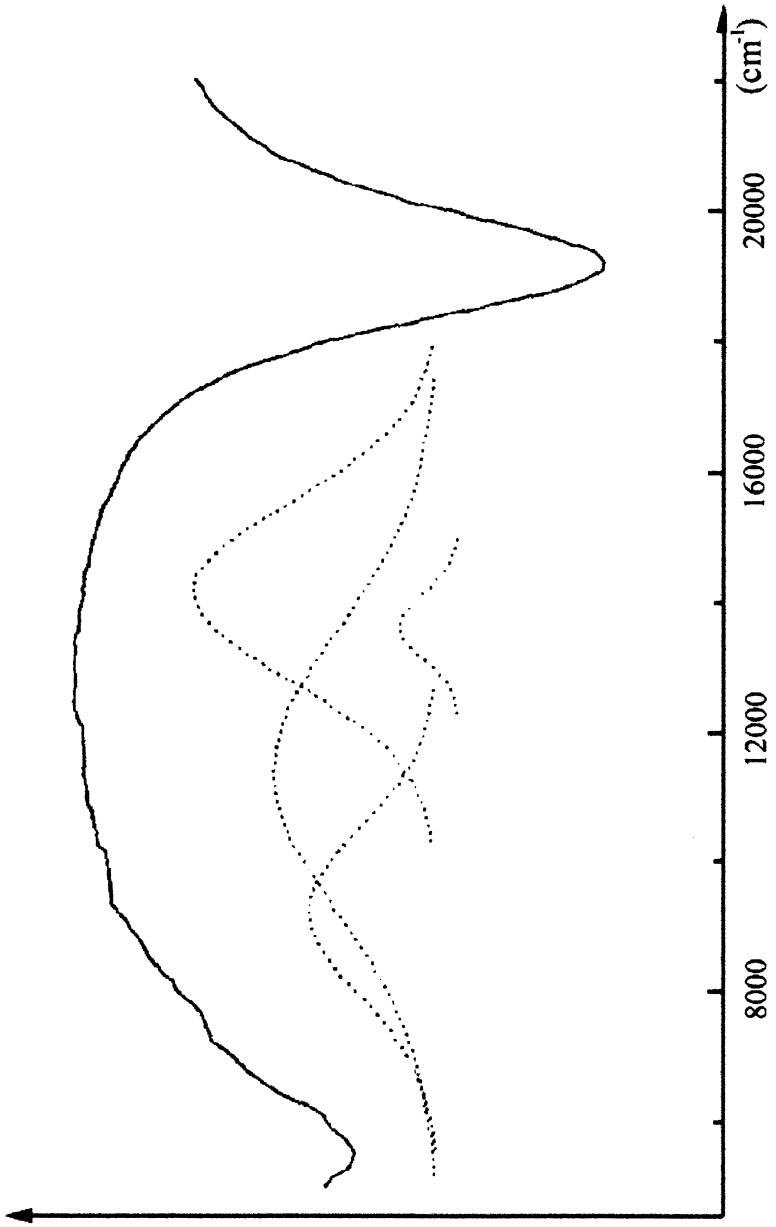

Figure 1. The electronic absorption spectrum (diffuse reflection spectrum) of the title complex recorded at room temperature in the region of 455 nm to 2000 nm (5000–22000 cm^{-1}), as drawn for the *d-d* spectrum.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

in lamp intensity using a carbon-black reference, and smoothed for noises. See Fig. 2.

RESULTS AND DISCUSSIONS

Description of the Object Crystal Structure

The space coordinate condition of [CuCl(L-Pro)(H_2O)] is shown in Fig. 3. The Cu atom displays distorted squarepyramidal coordination, with the H_2O, Cl^- and one amino-acid ligand in the basal plane and an O2 atom of another pro in the apical sites. The average Cu-O and Cu-N bond lengths are 1.936(6) and 2.006(8) Å[5]. To make it convenient in theoretical calculation, the structure was described in a pole coordinate system. The values are given in Table 1.

Theoretical Calculation and Spectrum Resolution

In accordance with the environment of [CuCl(L-Prolinato)(H_2O)], Table 1. Original data can be set up. We here considered our calculation upon strong field due to the low symmetry, which may bring about considerable *d*-electronic energy level splits accompanied by weak configuration interactions. In ligand field theory, Li Jianmin et al.[6,7] had suggested a non-free ion wave function radial theory and developed a program package (PLFT) for calculation of this ligand field theory. The parameters of crystal field and the energy level of the title complex were calculated with PLFT[2,6–10]. The values were given in the Table 2 and Table 3, respectively.

From the observed electronic absorption spectrum (Fig. 1), four strong absorption peaks lying at 9208, 11,386, 13,640, and 14,165 cm^{-1} are observed. They may due to the *d-d* transition absorption of Cu(II) ion and can be assigned as $^2A(dxy,e)\rightarrow{}^2A(dx^2-y^2,e)$, $^2A(dz^2,e)\rightarrow{}^2A(dx^2-y^2,e)$, $^2A(dyz,e)\rightarrow{}^2A(dx^2-y^2,e)$ and $^2A(dxz,e)\rightarrow{}^2A(dx^2-y^2,e)$, respectively. The electronic absorption spectrum and PAS of [CuCl(L-Prolinato)(H_2O)] showed almost the same absorption position and intensity in their common wavelength region. Peaks lying at 13,640 cm^{-1} and 14,165 cm^{-1} in the *d-d* absorption spectrum, which is nearly in agreement with 13,518 cm^{-1} and 14,220 cm^{-1} in PAS. Therefore, according to Table 3, the spectrum is not sharp peaks caused y split d-d energy gap and only appeared an overlapped broad band. resulted from the following reason: 1. Crystal grating vibration. 2. Jahn-Teller effect. 3. The low symmetry of the coordinate field.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

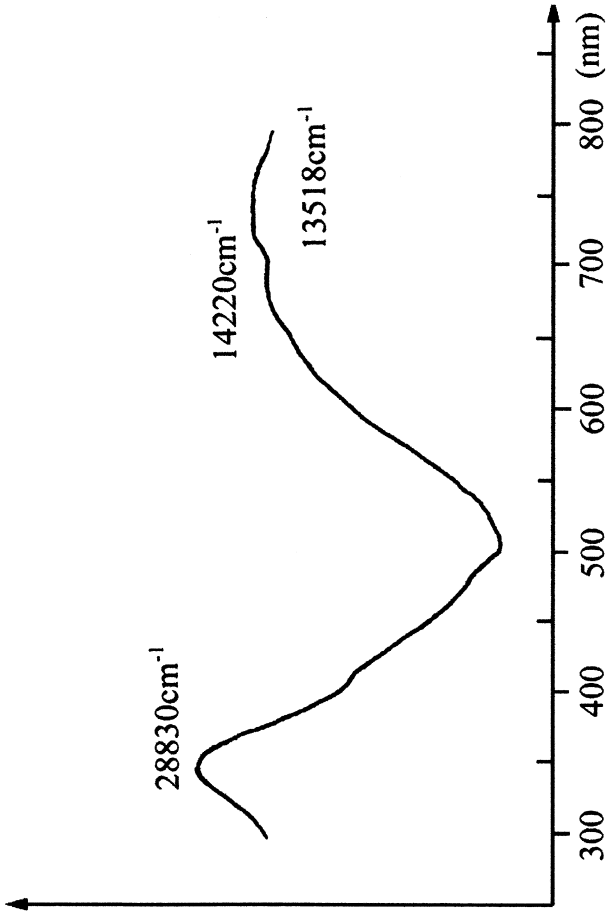

Figure 2. The corrected photoacoustic spectrum of the title complex as recorded between 300 nm and 800 nm region at room temperature.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

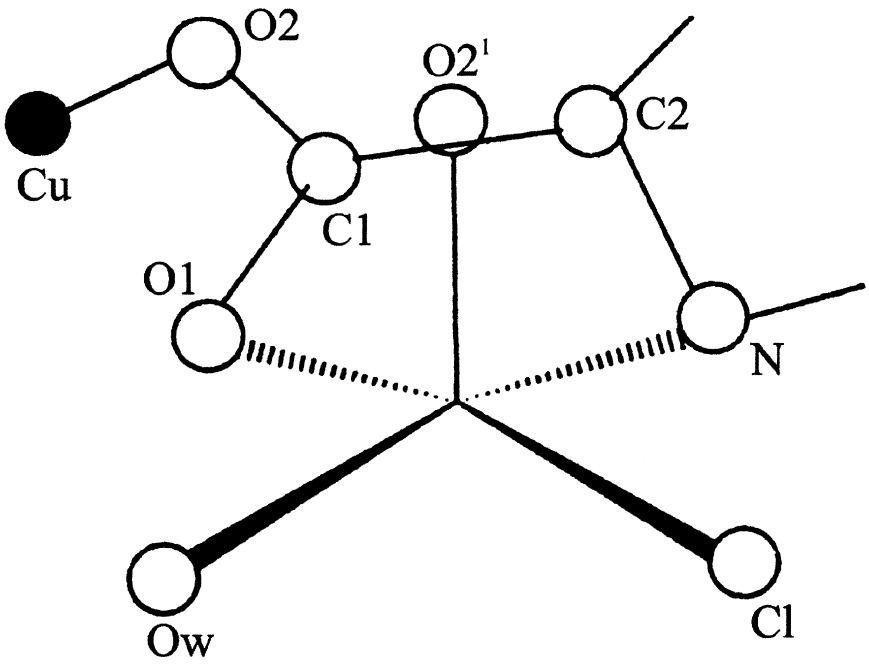

Figure 3. The space coordinate condition of [CuCl(L-Pro)(H_2O)].

Table 1. The Structure Data of [CuCl(L-Pro)(H_2O)]

	Cl	N	O1	Ow	O21
R(Å)	2.261	1.994	1.948	1.987	2.286
θ (deg.)	94.8	99.4	100.0	91.9	0.0
ϕ (deg.)	0.0	95.1	180.4	268.1	/

In addition, the broad band probably also imply that the high energy level which being relative to base state is sensitive to the band length between ligand and Cu(II).

As to the transition peaks which were less than 11400 cm^{-1} (see Table 3) had not been shown in the PAS because they have been out of the region that that spectrograph can record. The absorption peaks which wavelength were more than 800 nm in PAS cannot be measured.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table 2. The Crystal Field Parameters of [CuCl(L-Pro)(H_2O)]

Parameter	Value	Parameter	Value
μ (Debye)	1.25640	a1	0.58692
t	0.03367	a2	0.64063
Ω (Hartree)	0.17465	$\langle r^2 \rangle$ (a.u)	2.09631
$\tilde{N}^2$	0.97	$\langle r^4 \rangle$ (a.u)	12.05559
$p^{(2)}$	1.56053	$\langle r^{-3} \rangle$ (a.u)	5.66421
$p^{(4)}$	1.93597	B (cm^{-1})	1000
ζ_1	5.84097	C (cm^{-1})	3419
ζ_2	1.82692	ζ_{3d} (cm^{-1})	547

Table 3. The Electronic Adsorption Spectrum of [CuCl(L-Pro)(H_2O)]

Peak	Transition	Calc. (cm^{-1})	EAS (cm^{-1})	PAS (cm^{-1})
Γ1	$^2A(dxy,e) \rightarrow {}^2A(dx^2-y^2,e)$	9439	9208	
Γ2	$^2A(dz^2,e) \rightarrow {}^2A(dx^2-y^2,e)$	10,868	11,386	
Γ3	$^2A(dyz,e) \rightarrow {}^2A(dx^2-y^2,e)$	13,570	13,640	13,518
Γ4	$^2A(dxz,e) \rightarrow {}^2A(dx^2-y^2,e)$	14,259	14,165	14,220
				28,830

From the above analysis, we found that the spectroscopic properties, electronic structure and crystal structure of [CuCl(L-Pro)(H_2O)] are agreement with one another.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Liu Hongpu, for the assistance with the electronic absorption spectrum measured. This work was partly supported by the NATIONAL NATURE SCIENCE FOUNDATION OF P.R. CHINA.

REFERENCES

1. Lomozik, L.; Wojciechowska, A. Polyhedron **1989**, *8*, 1.
2. Li, J.; Xu, M.; Zhang, Y. Spectro. Lett. **1992**, *25* (4), 487.
3. Li, J.; Xu, M.; Huang, X.; Zhang, Y. Spectro. Lett. **1995**, *28* (1), 111.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

4. Yukawa, Y.J. Chem. Soc. Dalton Trans. **1992**, 3217.
5. Solans, X.; Ruiz-Ramiez, L.; Martinez, A.; Gasque, L.; Brianso, J.L. Acta. Cryst. **1988**, *C44*, 628.
6. Zhang, Y.; Li, J.J. Struct. Chem. (China) **1983**, *2* (2), 135.
7. Li, J.; Wang, J.; Xu, M.; Zhang, Y. Spectro. Lett. **1998**, *31* (6), 1255.
8. Zhang, Y.; Li, J.J. Molec. Sci (China) **1982**, *2* (4), 165.
9. Zhang, Y.; Li, J. J. Univ. Sci. & Tech. of China (China) **1982**, *12* (3), 74.
10. Xu, M. M.S. thesis in University of Science and Technology of China.

Received May 20, 2001
Accepted October 25, 2001

Request Permission or Order Reprints Instantly!