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SPECTROSCOPIC PROPERTIES AND ELECTRONIC STRUCTURE OF [CuCl(L-PROLINATO)(H₂O)]

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ABSTRACT

[CuCl(L-Prolinato)(H₂O)] 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)(H₂O)] electronic structure; PLFT

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INTRODUCTION

Metal proteins have great significance in life activities. Many metal proteins act as high selective and efficient catalysts in biological process in living bodies¹. 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 $[\text{CuCl}(\text{L-Prolinato})(\text{H}_2\text{O})]$.

EXPERIMENTAL

The title complex was prepared as reported⁴. 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 from 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 (HITACHI) V-34100 UV/VIS, which was made by ANHUI INSTITUTE OF OPTICS AND FINE MECHANICS CHINESE ACADEMY OF SCIENCE. Here only the region of $5000\text{--}22,000\text{ cm}^{-1}$ 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 monochromator 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



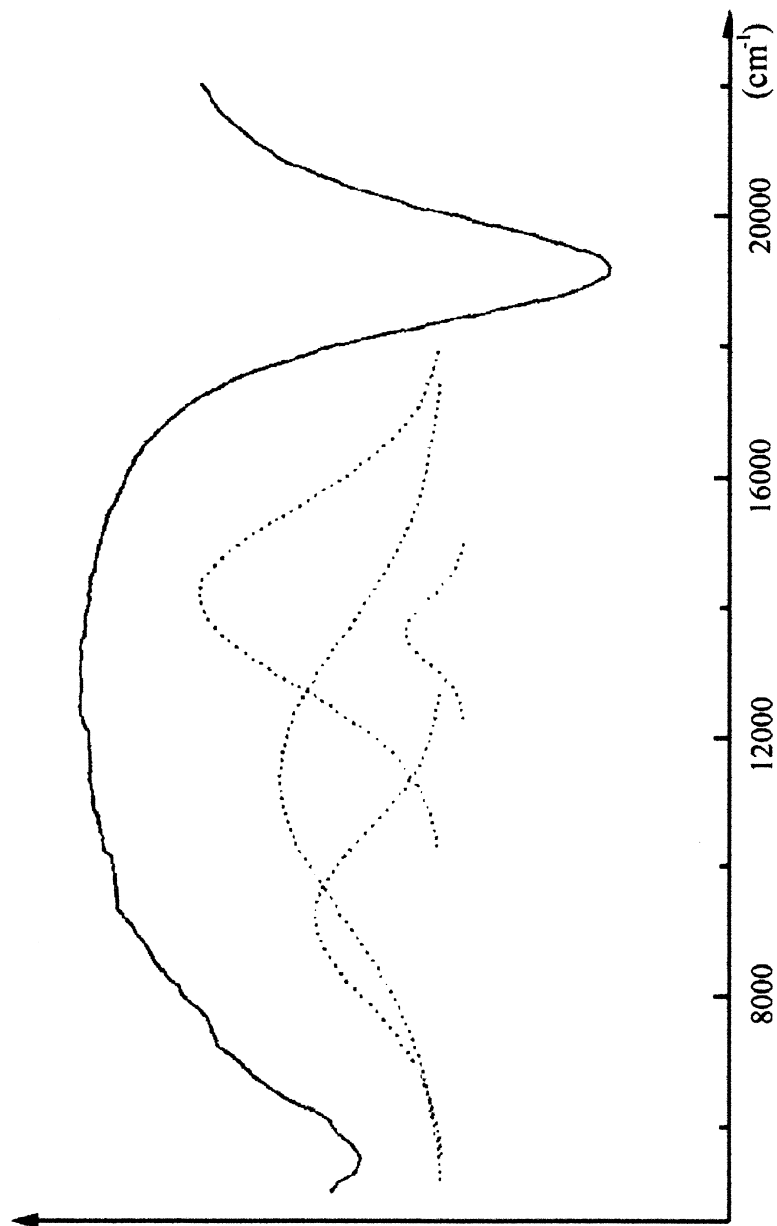


Figure 1. The electronic absorption spectrum (diffuse reflection spectrum) of the title complex recorded at room temperature in the region of 455 nm to 2000 nm ($5000\text{--}22000\text{ cm}^{-1}$), as drawn for the $d\text{-}d$ spectrum.

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 $[\text{CuCl}(\text{L-Pro})(\text{H}_2\text{O})]$ 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) Å⁵. 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 $[\text{CuCl}(\text{L-Prolinato})(\text{H}_2\text{O})]$, 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 $^2\text{A}(\text{dxy},\text{e}) \rightarrow ^2\text{A}(\text{dx}^2-\text{y}^2,\text{e})$, $^2\text{A}(\text{dz}^2,\text{e}) \rightarrow ^2\text{A}(\text{dx}^2-\text{y}^2,\text{e})$, $^2\text{A}(\text{dyz},\text{e}) \rightarrow ^2\text{A}(\text{dx}^2-\text{y}^2,\text{e})$ and $^2\text{A}(\text{dxz},\text{e}) \rightarrow ^2\text{A}(\text{dx}^2-\text{y}^2,\text{e})$, respectively. The electronic absorption spectrum and PAS of $[\text{CuCl}(\text{L-Prolinato})(\text{H}_2\text{O})]$ 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.



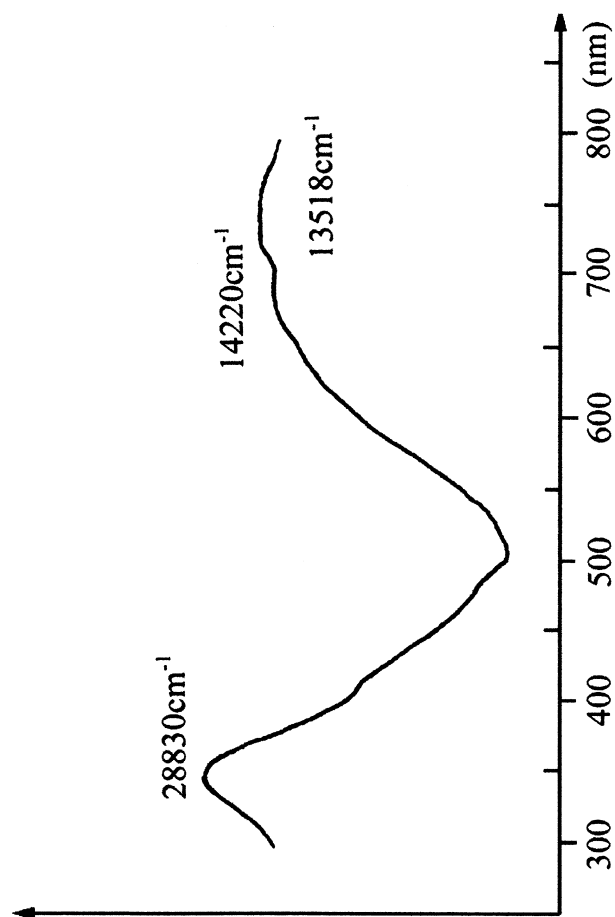


Figure 2. The corrected photoacoustic spectrum of the title complex as recorded between 300 nm and 800 nm region at room temperature.

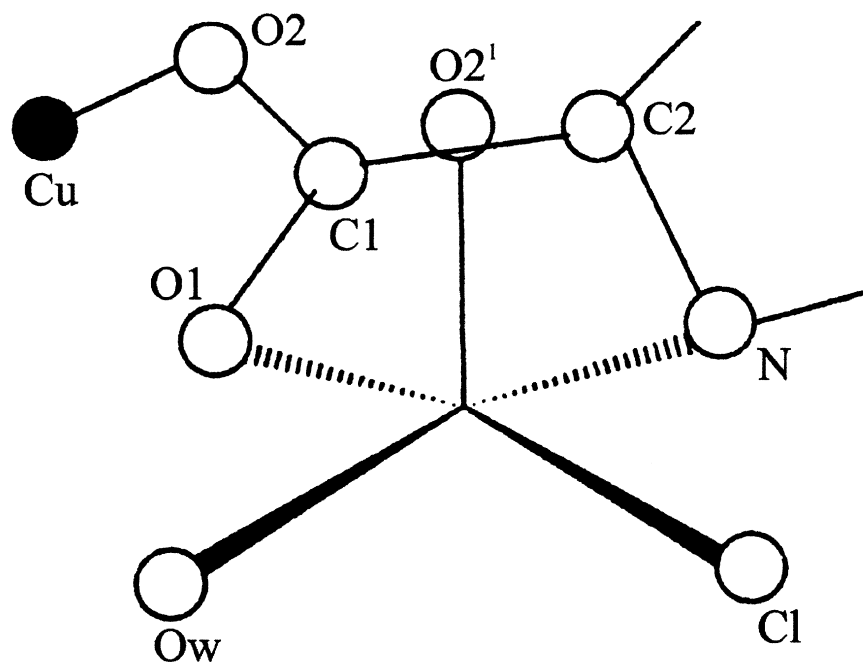


Figure 3. The space coordinate condition of $[\text{CuCl}(\text{L-Pro})(\text{H}_2\text{O})]$.

Table 1. The Structure Data of $[\text{CuCl}(\text{L-Pro})(\text{H}_2\text{O})]$

| | 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.



Table 2. The Crystal Field Parameters of [CuCl(L-Pro)(H₂O)]

| 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)(H₂O)]

| Peak | Transition | Calc. (cm ⁻¹) | EAS (cm ⁻¹) | PAS (cm ⁻¹) |
|------------|---|---------------------------|-------------------------|-------------------------|
| $\Gamma 1$ | ${}^2A(dx y, e) \rightarrow {}^2A(dx^2 - y^2, e)$ | 9439 | 9208 | |
| $\Gamma 2$ | ${}^2A(dz^2, e) \rightarrow {}^2A(dx^2 - y^2, e)$ | 10,868 | 11,386 | |
| $\Gamma 3$ | ${}^2A(dyz, e) \rightarrow {}^2A(dx^2 - y^2, e)$ | 13,570 | 13,640 | 13,518 |
| $\Gamma 4$ | ${}^2A(dxz, e) \rightarrow {}^2A(dx^2 - y^2, e)$ | 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)(H₂O)] are agreement with one another.

ACKNOWLEDGMENTS

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