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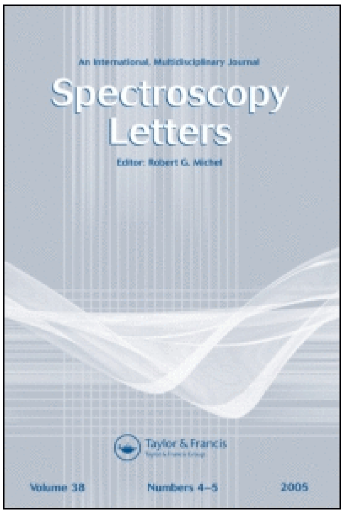

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Photoacoustic Spectroscopic Study on a Pair of Hydrate Isomers for Dinuclear Copper(II) Complexes

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PHOTOACOUSTIC SPECTROSCOPIC STUDY ON A PAIR OF HYDRATE ISOMERS FOR DINUCLEAR COPPER(II) COMPLEXES

Key words: Photoacoustic spectrum; Hydrate isomers; Dinuclear ligand.

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ABSTRACT

Photoacoustic spectroscopy has been used to measure the optical absorption of a pair of hydrate isomers of dinuclear copper (II) complexes with 26-membered hexa-aza-macrocycle. It is found that the absorptions of both isomers in the visible region are quite different, which indicates the diversity of their crystal structures. It is also shows that the difference on absorption properties of the studied isomers is difficult to distinguish by using other conventional spectroscopies.

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INTRODUCTION

It is well known that many active centers of proteins and biological enzymes are involved in bimetallic coordination, and several methods have been used to investigate the interaction mechanism of proteins or biological enzymes. One of the important ways is to mimic the structures of the active centers for proteins, that is, to synthesize model complexes of the active site in the native enzymes and then systematically study their structures as well as the chemical and physical properties.

In the aspect of designing the models, dinuclear ligands play a significant role. According to the structural feature of the active centers of proteins or enzymes, one can obtain desired models by designing macrocycles with specific structures and making them to coordinate with metal ions, which can be bound by a bridging linkage group. Thus, it is very important to investigate the structures of the dinuclear ligand compounds. In this paper, photoacoustic (PA) spectroscopy has been employed to measure the optical absorption of a pair of hydrate isomers of dinuclear copper (II) complexes with 26-membered hexa-aza-macrocycle.

The dinuclear ligand compounds in the study are a pair of hydrate isomers with the formula $LCu_2(CH_3COO)_2(H_2O)_2(ClO_4)_2$. One of them is a violet compound, as

$$[Cu_2(C_{24}H_{38}N_6)(CH_3COO)_2](ClO_4)_2(H_2O)_2$$

whose water molecules are outside the complex. The other is a blue compound, as

$$[Cu_2(C_{24}H_{38}N_6)(CH_3COO)_2(H_2O)_2](ClO_4)_2$$

and the water molecules are inside the complex. The unique difference between both isomers is the position of the water molecules. It is worthily pointed out that hydrate isomerism of coordination compounds is a widely known but seldom observed phenomenon. One of the most famous examples is $CrCl_36H_2O$ which has three hydrate isomers[1], but no such hydrate isomers accommodated in a macrocycle have been reported.

Generally, the absorption and reflection spectroscopies might be used in measuring the optical properties of the compounds. It must be pointed out that both of the blue and violet isomers in solution show an identical absorption signal. This can be interpreted that both isomers quickly interchange with the solvent and get to equilibrium in solution at room temperature. Therefore, in order to clarify the different structures by using the measurement of absorption properties of both isomers, they must be measured in the solid state. However, absorption spectroscopy is limited for the solid powders because of the nontransparent and highly tscattering properties of the powders. Diffuse reflection spectroscopy for powders is not very sensitive. Thus taking the advantage of PA spectroscopy to measure the absorption of the two solid powder samples provides the best alternative.

EXPERIMENTAL

1. Syntheses of the Complexes

The blue isomer: The solution of L (103mg, 0.25mmol, in 5ml acetonitrile) is added to a solution of $Cu(OAc)_2{\cdot}H_2O$ (100mg, 0.5mmol, in 2ml water) with stirring; then five drops of a saturated aqueous solution of $NaClO_4$. The resultant solution is left to stand at -5°C. After two days, the blue prisms one obtains are filtered and washed with acetonitrile, then dried in a desiccator containing silica gel.

The violet isomer: With a similar procedure as above, except in the final procedure 5ml of n-butyl alcohol is added, and then left to stand at room temperature. Two days later, the violet isomer is obtained.

Both isomer components are confirmed by IR spectra and elemental analysis, and their space structures are determined by X-ray crystallography.

2. Photoacoustic Spectra

The PA spectra for both isomers are recorded at room temperature in the region of 400-800 nm, which are measured by a homemade single-beam spectrometer[2]. A 500 W xenon lamp and a PA cell with an electret microphone are used. The chopping frequency is 12 Hz. After preamplification, the output of the microphone is fed to a Lock-in-amplifier. The signals are normalized using a carbon-black reference. In order to prevent PA saturation, the samples are diluted using SiO_2 at a rate of 1:10.

In Figure1, the A and B show the PA spectra of the violet isomer and blue isomer, respectively. From this we can see that the PA signals of both isomers in the visible region are obviously different.

RESULTS AND DISCUSSION

1. Absorption Properties

In principle,[3,4] the maximum number of d-d transitions in the electronic spectrum of a copper(II) complex is four, in practice, very few complexes give some indication of more than two bands. Many complexes yield spectra involving two clear bands, or show a main band with a possibly resolved shoulder, and many others reveal a single broad absorption band. A mean energy value of all four d-d transitions is taken as the band energy when only one band is observed, but the weighted mean is taken if more than one band is observed. Hathaway [5] pointed out that it is possible to predict the stereochemistry of the local copper(II) ion environment in copper(II) complexes from the position and intensities of d-d transition bands of CuX_4 or CuX_6 chromophores. The energy ranges covered by the d-d transition bands of CuN4-6 chromophores of different stereochemistry, including an indication of the tetragonal distortion, were also listed [5].

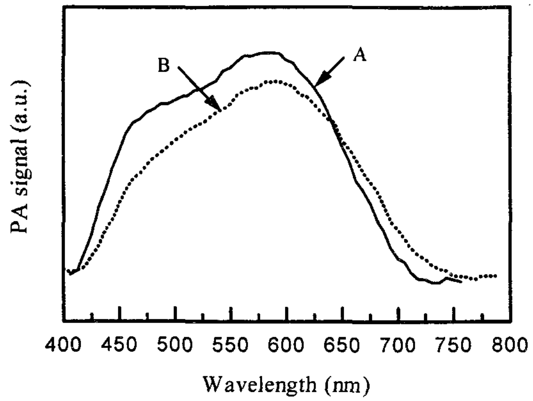

Figure 1. PA spectra of a pair of hydrate isomers. A: for the violet isomer, B: for the blue one.

Based on Hathaway' work, we conclude that there are two absorption maxima clearly observed from the spectrum A in Figure 1 for the violet isomer. The band at 584 nm (1.712×10^4 K, K is the wavenumber) is assigned to the transitions

$$d_{xy} \rightarrow d_{x^2-y^2} \qquad (1)$$

and a resolved shoulder band at 494 nm (2.024×10^4 K) corresponds to the blend transitions in distorted square-planar symmetry

$$d_{z^2} \rightarrow d_{x^2-y^2} \qquad 2(a)$$

and

$$d_{yz}, d_{xz} \rightarrow d_{x^2-y^2} \qquad (2b)$$

which indicates that the metal atoms in the violet isomer are in square-planar geometry with the N3O chromophore and are not coordinated by the water molecules.

Shown by spectrum B in Figure 1 is the PA spectrum of the blue isomer, from which we can see that the two absorption maxima cannot be clearly distinguished. Hathaway and coworkers [5,6] have extensively studied the copper (II) with square-pyramidal geometry by the electronic spectrum. They pointed out that, generally, the coordination geometry of five coordinated cooper(II) are in trigonal bipyramid if there is a single band in the range of $(1.250 \pm 0.150)\times10^4$ K or in square pyramid if there is one or two absorption bands in the range of $(1.500 \pm 0.200)\times10^4$ K. Referring to their works, we can conclude that the band at 606 nm (1.650×10^4 K) for the blue isomer is assigned to

$$d_{z^2} \rightarrow d_{x^2-y^2} \tag{3a}$$

and

$$\mathrm{d}_{xy} \rightarrow \mathrm{d}_{x^2-y^2} \tag{3b}$$

blend transitions for a square-pyramidal system, which demonstrate that the two copper atoms in the blue isomer have N_3O_2 square pyramidal coordination environment and are coordinated by the water molecules. On the other hand, there is a poorly resolved shoulder at about 520 nm (1.923×10^4 K), which indicates that there is some square-planar feature for the chromophore in the blue isomer. The result agrees well with that of the crystal structure determination of the compound where the axial ligation of the water molecule is quite weak (Cu-O bond length ~2.5Å) and the copper atoms are considered nearly to be as the square-planar configuration.

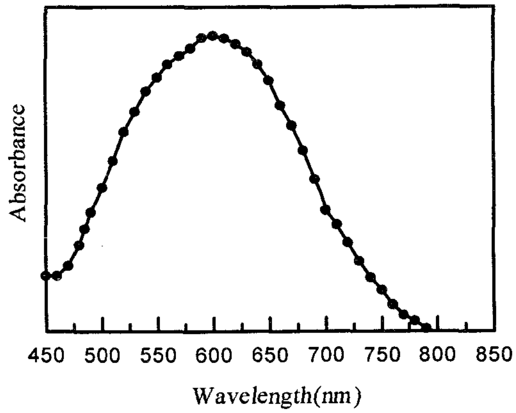

Figure 2. Electronic spectra of the two isomers in 1:4 aqueous and acetonitrile.

Figure 2 shows the electronic spectra of the two isomers in a 1:4 water and acetonitrile solution at 25°C. From it we can see that both the blue and violet isomers show identical absorption properties with a broad band at 598 nm (16.72kK). It can be interpreted that both complexes quickly interchange and get to balance in the solution at room temperature.

2. X-ray Crystal Structure Determination

In order to confirm the discussion above, the molecular structures of the two isomers, obtained from the X-ray crystal structure determination, are showed in Figure 3, with the hydrogen atoms omitted for clarity.

From Figure 3(a) we can see clearly that each of the two copper atoms (Cu(1) or Cu(2)) in the violet isomer is four-coordinated by three nitrogen atoms and one oxygen atom forming a distorted square-planar symmetry. All four atoms coordinated with each copper atom are from the macrocycle, and the oxygen atoms (O(1) or O(2)) of water molecules are not banded with copper atoms.

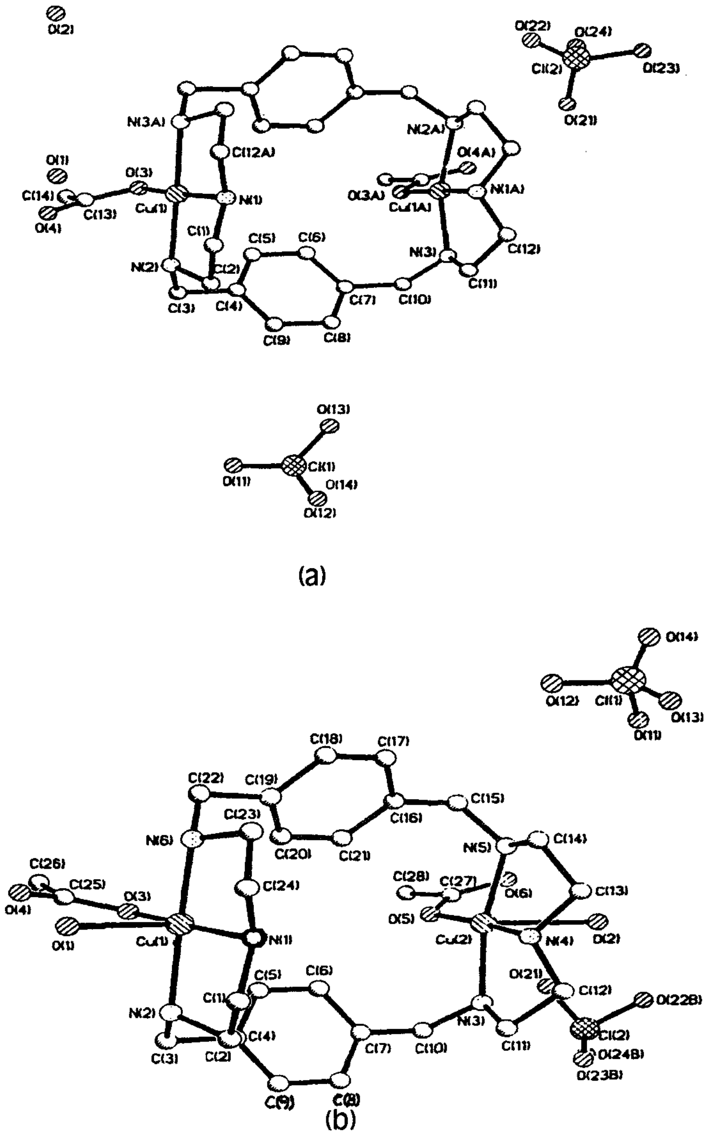

Figure 3. Molecular structures of the two isomers with the hydrogen atoms omitted for clarity. (a): for the violet isomer; (b): for the blue one.

Figure 3(b) indicates that each atom in the blue isomer is five coordinated with the N_3O_2 chromophore forming a square- pyramidal geometric formation. The three nitrogen atoms with one oxygen atom come from the macrocycle and the other oxygen atom (O(1) or O(2)) is from the water molecules.

We can see that the unique difference between the molecular structures of the both isomers is the position of the water molecules. This structure difference is obviously indicated by the PA spectrum of the both isomers.

CONCLUSION

From the discussion on PA spectra and by referring to the determination of crystal structure, we have concluded that the metal atoms in the blue isomer are in square pyramidal geometry with the N_3O_2 chromophore and are coordinated by the water molecules. Both of the two copper atoms in the violet isomer have N_3O square planar coordination environments, and are not coordinated by the water molecules. On the other hand, we also see that the PA spectroscopy is a very effective method to measure the absorption properties of these solid powder samples. In practice, the results gained in this paper from PA spectra are difficult to obtain by using other conventional spectroscopic techniques.

ACKNOWLEDGMENTS

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