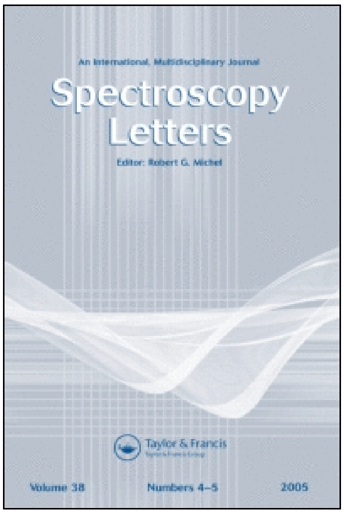

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectroscopic and Structural Studies of Complex of $[CU(DIEN)(CNGE)(ONO_2)_2]$ (Dien=Diethylenetriamine, CNGE=Cyanoguanid)

Xu Haitao[a]; Zheng Nengwu[a]
[a] Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, P. R. China

To cite this Article Haitao, Xu and Nengwu, Zheng(2000) 'Spectroscopic and Structural Studies of Complex of $[CU(DIEN)(CNGE)(ONO_2)_2]$ (Dien=Diethylenetriamine, CNGE=Cyanoguanid)', Spectroscopy Letters, 33: 2, 185 — 194
To link to this Article: DOI: 10.1080/00387010009350068
URL: http://dx.doi.org/10.1080/00387010009350068

SPECTROSCOPY LETTERS, 33(2), 185–194 (2000)

SPECTROSCOPIC AND STRUCTURAL STUDIES OF COMPLEX OF [CU(DIEN)(CNGE)(ONO$_2$)$_2$] (DIEN=DIETHYLENETRIAMINE,CNGE=CYANOGUANID)

key words: electronic absorption spectrum, copper complex,
ligand field theory and structural studies

Xu Haitao , Zheng Nengwu

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

ABSTRACT

The electronic absorption spectrum (diffuse reflection spectrum) of the crystal of [Cu(dien)(cnge)(ONO$_2$)$_2$] has been measured. The experimental results are interpreted quantitatively with ligand field theory and the radial wave function of non-free copper (II), and our calculation values coincide well with the

experimental results. As a result, the d-d absorption spectrum was explained satisfactorily. In particular, the structural characterizations whose degree of distortion of crystal structures of three Copper(II) complexes is different in this paper, are also discussed with their spectral behaviors. The experimental data provides significant correlation between the spectra and degree of distortion of coordination structures.

INTRODUCTION

Copper is an important trace element in almost all forms of life, and it is the third most abundant element in the human body, following iron and zinc. Copper containing metalloenzymes are now known to be involved in a variety of biological functions; such as electron transfer, copper storage and many oxidase activities[1]. Anomalies in copper metabolism in humans, whether caused by a deficiency of, or an inability to absorb the metal, can lead to the development of Menke's disease [2-4]. Near normal growth rates and survival of animal models for this disease have been achieved by the administration of copper(II) salts. The nature of the copper complexes present in the system is not fully understood.

To obtain more information on the structure of the complexes, much detail work about the correlation between the spectrum and coordination structure has been done. Since the electronic absorption spectra of complexes are the base of the studies of electronic structure of their crystal and the spectroscopic properties may be as a bridge that links the crystal structure and the electronic structure, it is thought meaningful to export correlation between features appearing in alternative spectra of copper complexes and their structure. So, not only the electronic absorption spectrum of the crystal of $[Cu(dien)(cnge)(ONO_2)_2]$ has been studied, but also it has been compared reasonably with another two spectrums of Copper(II) complexes, whose degree of distortion of crystal structures is different. It exemplified the idea that the electronic absorption spectrum of the crystal, relevant to the electronic structure, depended on the interaction of metal ions with ligand ions. Simply stated, the electronic absorption spectrum of the crystal must indicate the degree of distortion of the crystal structures, as demonstrated in this paper. Our work makes it possible to obtain more structural information from the electronic absorption spectrum.

EXPERIMENTAL

An aqueous solution (10 cm^3) of $Cu(NO_3)_2.3H_2O$ (0.50g, 2.07 mmol) was added to an aqueous solution (10 cm^3) containing dien (0.222g,20.7 mmol), and cnge (0.175g, 2.08 mmol). The resulting blue solution was heated to 90 ^0C for half an hour. Solvent volume was reduced, ethanol was added and the mixture was left at 5 ^0C for 16 h. After recrystallization from aqueous ethanol, the blue crystal was obtained[5]. Elemental analysis was measured using a PERKIN-ELMER MODEL 240 C and the observed values were found approximately equal to calculated values.

The electronic absorption spectrum (diffuse reflection spectrum) of $[Cu(dien)(cnge)(ONO_2)_2]$ crystals were measured at room temperature in the region of 200-2500 nm using an HITANCHI V-34100 UV/VIS made by ANHUI INSTITUTE OF OPTICS AND FINE MECHANICS CHINESE ACADEMY OF SCIENCE. The results measured and the computer resolution of overlapping electronic absorption bands are curved and shown in Figure 1.

RESULTS AND DISCUSSIONS

Discussions about the crystal structure and the spectra properties of $[Cu(dien)(cnge)(ONO_2)_2]$

In the crystal structure of $[Cu(dien)(cnge)(ONO_2)_2]$, the Copper(II) ion coordination, as a distorted square bipyramid with NO_3 occupying an axial

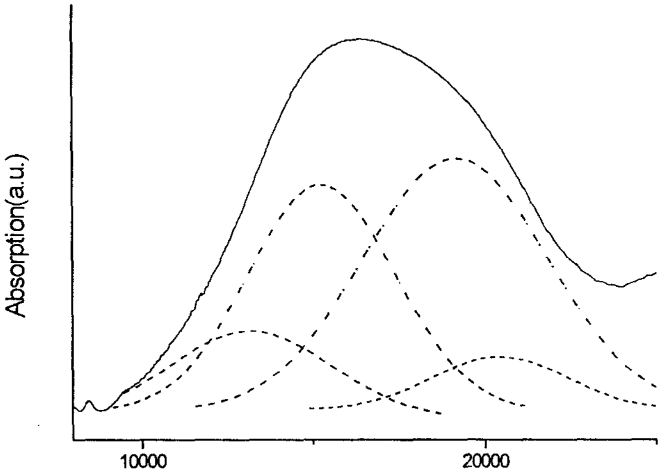

FIG.1. The electronic absorption spectra of the title complex. Absorption versus cm-1.

position is clearly seen in Figure1. The coordination number of the Copper(II) ion is six, three N atoms come from dien, another N atom is provided by cnge. We chose Cu-O(22) as the Z-axis of the title crystal. Four N atoms are in an approximate flattened plane, as shown in Figure 2. The data of the structure is listed in Table 1. So, the approximate symmetry of the crystal structure of $[Cu(dien)(cnge)(ONO_2)_2]$ is C_1.

According to ligand field theory, Li Jianmin had suggested a non-free ions wave function radial scaling theory for which a software program package (PLFT) had been developed and the radial wave function of Cu(II) can be written in double ζ [6,7] as,

$$R(r, \Omega) = C^{-1/2}[0.55428STO(\zeta_1)+0.60500STO(\zeta_2)]$$
$$= a_1STO(\zeta_1)+a_2STO(\zeta_2)$$

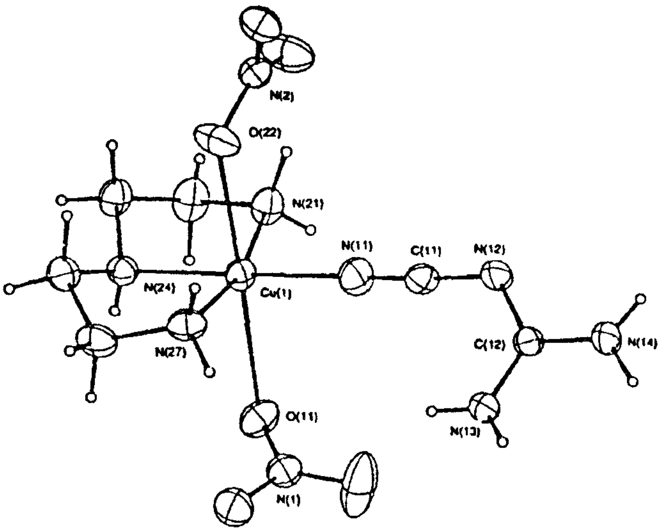

FIG. 2a. Molecular structure of the complex.

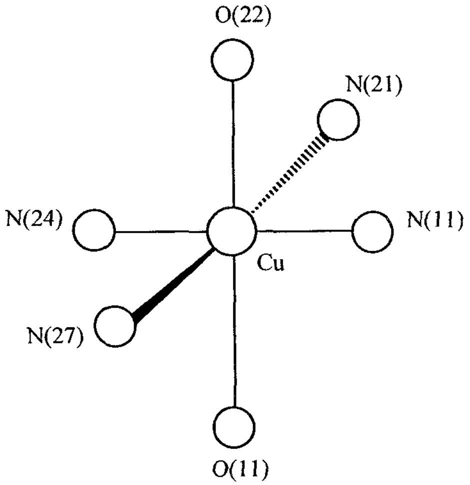

FIG. 2b. Coordinate structure of Cu(dien)(cnge)(ONO$_2$)$_2$

TABLE 1.

The structural data of the crystal.

Atom	O(22)	O(11)	N(11)	N(21)	N(24)*	N(27)
R(Å)	2.517	2.567	1.945	2.006	1.988	2.019
θ(deg.)	0.0	173.0	88.7	89.8	91.0	81.9
φ(deg.)	0.0	263.0	0.0	95.2	1179.5	263.3

where $\zeta_1 = 6.3496(1-0.41500\Omega+0.25000\Omega^2)$

$\zeta_2 = 2.5250(1-1.64500\Omega+0.35500\Omega^2)$

where C is the normalization coefficient, and Ω is the so-called scale of non-freedom which is the variable parameter determined by: the number of ligands, average bond length, the ratio of dipole length and length {t}, and the average dipole moments of ligand(u), to describe the deviation-free ion.

Using the data in Table 1, the original data file can be set up by using the environment of Cu(II) and the coordinate system. The parameters of the crystal field and the electronic energy of the crystal can be calculated by using the PLFT. The calculated values are listed in Table 2 and Table 3. The observed values in Table 3 are results of the resolved absorption.

According to the observed d-d transitional spectrum (Fig. 1.) and data of the electronic absorption spectrum (Table 3) , we had known that the results, which are calculated assuming a strong ligand field because of very low symmetry, coincide well with the experiment values . Four absorption peaks lying at 13174, 15253, 19161, 20441 cm^{-1} and assigned as transition $^2A(^2Eg_a, e) \rightarrow {}^2A(^2Egb,e)$, $^2A(^2T_{2gc}, t) \rightarrow {}^2A(^2Egb,e)$, $^2A(^2T_{2gb}, t) \rightarrow {}^2A(^2Egb,e)$, $^2A(^2T_{2ga}, t) \rightarrow {}^2A(^2Egb,e)$ are

TABLE 2.

The crystal field parameters of the crystal.

$\bar{\mu}$ (Debye)	1.16867	a1	0.59331
Ω (Hartree)	0.20534	a2	0.64760
$\tilde{N}$	0.975	$<r^2>$(a.u.)	2.38825
$P^{(2)}$	1.74700	$<r^4>$(a.u.)	15.92995
$P^{(4)}$	2.19200	$<r^{-3}>$(a.u.)	5.36986
ζ_1	5.74158	B (cm^{-1})	942
ζ_2	1.70989	C (cm^{-1})	3228
$\bar{t}$	0.05018	ζ_{3d} (cm^{-1})	513

where B and C are Recah's parameters, ζ_{3d} represents spin-orbital coupling constant, and $p^{(2)}$and $p^{(4)}$ are polarization factors, defined by us.

TABLE 3.

Data of the electronic absorption spectrum

	Cal	Obs
${}^2A({}^2Egb,e)$	0.	0.
${}^2A({}^2Eg_a, e)$	12807	13174
${}^2A({}^2T_{2gc}, t)$	15606	15253
${}^2A({}^2T_{2gb}, t)$	19589	19161
${}^2A({}^2T_{2ga}, t)$	20072	20441

observed, respectively. From the spectral selection rules in the complex, the forbidden parity does not exist. As to the transition from the ground state ^2A to the higher energy state ^2A, it has four strong absorption peaks due to the rule of spin forbidden being canceled.

TABLE 4

The structure data of the crystal of [Cu(L-gly)$_2$•H$_2$O] •H$_2$O and [Cu(L-ArgH)$_2$(Ac)$_2$] •3H$_2$O

(B) Atom	O2	O4	O1	O3	O5	N
R(Å)	2.299	2.588	1.961	1.981	1.991	1.998
θ(deg.)	0.00	149.91	101.06	94.09	89.19	93.63
φ(deg.)	0.00	176.94	83.67	176.94	267.21	0.00
(C) Atom	O(5)	N(6)	N(2)	O(3)	O1	N(4)
R(Å)	2.570	2.884	1.996	1.938	1.936	1.991
θ(deg.)	0.00	176.70	91.00	94.20	87.40	95.20
φ(deg.)	0.00	126.40	98.5	181.80	0.00	275.90

TABLE 5

Data of the electronic absorption spectrum

	Cal			Obs		
	A	B	C	A	B	C
γ_1	12899	9462	12284	13174	9385	12100
γ_2	15606	11453	15438	15253	11751	14538
γ_3	19589	14164	18015	19161	13959	17216
γ_4	20072	15203	19488	20441	15599	20532

where A,B,C represent the crystals of [Cu(dien)(cnge)(ONO$_2$)$_2$] ,[[Cu(L-gly)$_2$] •H$_2$O] •H$_2$O and [Cu(L-ArgH)$_2$(Ac)$_2$] •3H$_2$O respectively .

Comparison of spectra of three crystals of different degree of distortion of crystal structures

In this paper, in order to obtain more information about correlation of structure and spectra, we have compared the structural and spectroscopic features of [Cu(dien)(cnge)(ONO$_2$)$_2$] with those of [[Cu(L-gly)$_2$]•H$_2$O]•H$_2$O[8] and [Cu(L-ArgH)$_2$(Ac)$_2$]•3H$_2$O[9]. Their structure coordination figures are very similar, and their coordination number is six. The structure data and the energy level of the crystals are listed in Tables 4 and 5, respectively .

From Table 1 and Table 4, the structural features of three little crystals in the equatorial plane is approximately the same, but their bond lengths in the Z axial dimension are apparently different. The farther the atom in the Z axial dimension is from equatorial plane , the higher energy level it is shifted to. The bond length of B in the Z axial dimension < the bond length of A in the Z axial dimension < the bond length of C in the Z axial dimension. γ_4(B) <γ_4(A)< γ_4(C) . It may be that the farther the atom in the Z axial dimension is from equatorial plane, the weaker the copper(II) ion is acted upon by the electrons of atoms in the Z axial dimension, and the stronger the copper(II) ion is acted by the electrons of atoms in the equatorial plane. A ligand field that centers the Copper(II) ions is more closely described as a square field. As the symmetry degrades, the split strength of the planar square field is much larger than that of the octahedral field. Note that the difference(γ_4-γ_3) of C > difference(γ_4-γ_3) of B > difference(γ_4-γ_3) of A at a high energy level. This occurs because the two bond length difference in the Z axial dimension of C > difference of the two bond length difference in the Z axial of dimension of B > difference of two bond length difference in the Z axial dimension of A. Note also that the symmetry of the C crystal is lower than that of the B crystal, and symmetry of the B crystal is lower than that of the A crystal. These results are in agreement with the Jahn-Teller effect. So here we have obtained a satisfactory result under the central potential field approximation, and the ideal model structure of the crystal has been reported.

Acknowledgment

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

References

1. Berrtini I., Gray H. B., Lippard S. J. and Valentine J. SS., Bioinorganic Chemistry, p. 3. University Science Books, California (1994)
2. Menks J. H. , Alter H., Steigleder G. K., Weakley D. R. and Sung J. H., Pediatrics 1962; 29: 764.
3. Danks D. M., Stephens B. J., Campbell P. E., Gillespie J. M., Walker-Smith J., Blomfield j. and Turner B., Lancer 1972; 1:1100.
4. Danks D. M., CampbelP. E. l, Stephens B. J., Mayne V. and Caartwright E., Pediatrics 1972; 50: 188.
5. Michael J. Begley, Peter Hubberstey and Jo Stroud Polyhedrom 1997; Vol 16. No. 5. pp. 805-813
6. Yongfen Zhang,and Janmin Li, J. Struct. Chem. (China) 1983; 2:189.
7. Rongchun Zhang, and Jianmin Li. J. Chin. Univ. S. Ci. Technol. (China) 1982 ; 12:74.
8. Li Jianmin, Ge Cunwang, Fang Jifa Cryst. Res. Technol. 1990; 25(4): K82-K86
9. Li Jianmin, Xu Ming, Yang Min, Zhang Yugen Spectroscopy Letters 1996 ; 29(1): 117-125

Date Received: September 12, 1999
Date Accepted: October 25, 1999