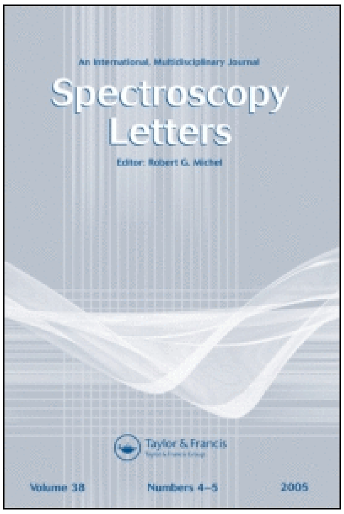

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Spectra, Magnetic Property and Coordination Structure Study on Polymeric Copper(II) Iodo Complex of Diethylenetriamne

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Spectra,magnetic property and coordination structure study on polymeric copper(II) iodo complex of diethylenetriamine

Key words:electronic absorption spectrum,photoacoustic absorption spectrum,ESR, $[Cu(diethylenetriamine)I_2]_n$,ligand field theory

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ABSTRACT

Polymeric $[Cu(dien)I_2]_n$ (dien=diethylenetriamine) was prepared.Its electronic absorption spectrum and photoacoustic spectrum were recorded at room temperature.They were compared with each other and the results were discussed quantitatively with respect to ligand field theory (LFT) and the radical scaling wave function of a non-free copper(II) ion.The theoretical values are in agreement with the observed ones.In addition,the ESR spectra of the title complex were measured at 77k and room temperature,respectively.They were compared with each other and characterized.Therefore,the electronic structure was also investigated with its spectra behaviors and PLFT.The spectra and the theoretical analysis about the title complex suggest there is a weak interaction between the Cu-Cu.It can be interpreted with using Kahn's theory.The g(= 2.0942) is greater than 2.040,conforming to a ground state configuration with unpaired electron in the $d_{x^2-y^2}$ orbital.

INTRODUCTION

The preparation and investigation of dinuclear Cu(II) complex draws from three quarters.First,there is a widespread occurrence of dinuclear Cu centers in biology[1,2].In particular,the occurrence of a pair of copper ions at the active site of the various forms of the oxygen carrier protein hemocyanin in many species of arthropods and mollusks has stimulated much interest in modeling the active-site structure,physicochemical properties,and function of this protein by the use of model complexes[3-7].Second,there are few spectroscopic properties reported about copper(II) complexes with coordinated iodide.Third, there is a need to understand the factors that are responsible for the magnetic exchange interactions between coupled copper ions[3,8].

For the purpose above,in this paper,we report the electronic absorption spectrum,ESR and PAS of the title complex.Electronic absorption spectra(EAS) and ESR were helpful in this group's work as a basis for studying the electronic structure of complexes[9,10].The choice of photoacoustic absorption spectra(PAS) in this group's recent work was made by considering the fact that there are synthetic difficulties in preparing crystals for all complexes, whereas PAS are advantageous in that they can be used for general solids[9-11]. In addition,PAS is capable of detecting very weak absorption[12] and magnetic exchange interaction between coupled metal ions.

EXPERIMENTAL

1:Preparation

A solution of 1.1 ml (10 mmol) of the ligand in 10 ml H_2O was added to a solution of 2.54 g (10 mmol) $CuSO_4\cdot 5H_2O$ in 10 ml water.The solution turned deep blue,characteristic of complexed copper(II) ions.After 10 min of continuous stirring,3.9 g (23.5 mmol) KI in 25 ml water was added.The deep blue color of the solution intensified,and a small quantity of gray-brown precipitate formed.The solution was stirred vigorously for a further 1.5 h and then filtered to remove the gray-brown solid.Approximately 30 ml ethanol were added to the filtrate.After two days at room temperature,very large dark green diamond shaped crystals were obtained.The crystals were separated,washed with ethanol,and air dried.According to our elemental analyses,infrared spectrum and the reference[13],we confirm it is the title complex.

2:Physical Measurements

Solid-state(diffuse reflectance,350-2500nm) "d-d" transition spectra were recorded on a Cary 2390 UV-VIS-NIR Spectrophotometer at room temperature.See fig.1.

ESR spectra were measured on a ER-200D-SRC EPR spectroscopy (Bruker Corp.) with the sensitivity S/N=220:1(Weak Pitch sample),resolution power 9mG(TCNQ sample),modulated frequency 100KHz and time constant 0.5s.The magnetic field was calibrated with a DPPH marker.The spectra of a powdered sample of the title complex were collected at room and liquid nitrogen(77K) temperatures.See fig.3.

As to the PA spectrometer,excitation source is 500W Xenon lamp with a CT-30F monochromafor in the region of 300-800nm.The light source intensity was modulated with a variable speed mechanical chopper at frequency of 12HZ.The room temperature photoacoustic signal was detected with a electret microphone. The output signal was normalized for the changes in lamp intensity by a referance of carbon black and was smoothed for noise.See fig.2.

In order to compare with the monomeric complex, $[Cu(dien)I_2]$ was preparated according to the ref.[13].Its electronic spectrum,PAS,ESR were recorded at room temperature,respectively.See fig.1-fig.3.

RESULTS AND DISCUSSION

1:Description of Structure

The structure of the title complex is shown in the fig.4[13].The geometry about each copper(II) center is axially elongated (4+2) octahedral,the equatorial ligating atoms being three nitrogen atoms from the dien ligand and one iodide ion (I(1)),while the axial sites are occupied by the chain-propagating I(2) ions.The copper center lies on a mirror plane which bisects the dien ligand,passing through N(2),and also contains atoms I(1) and I(2).Principal distances and angles in the cation are listed in the table 1[13].The structure of monomer and its principal bond lengths,angles are also listed in the fig.4 and table 1,respectively[13].

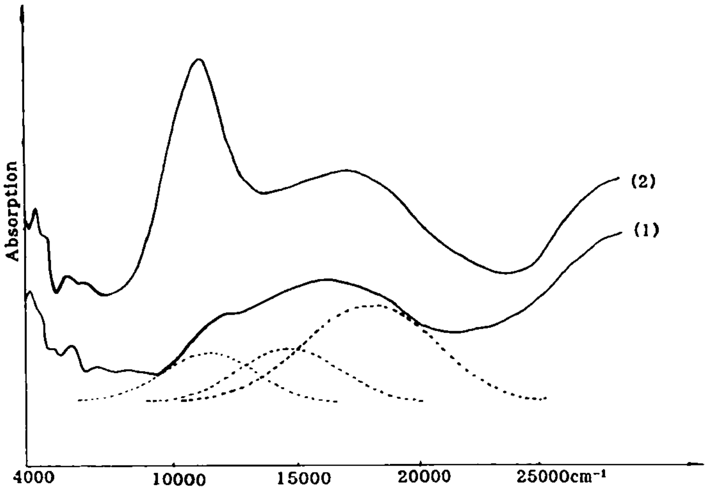

Fig.1: EAS of polymeric[Cu(dien)I_2]$_n$(1) and EAS of monomeric[Cu(dien)I_2](2)

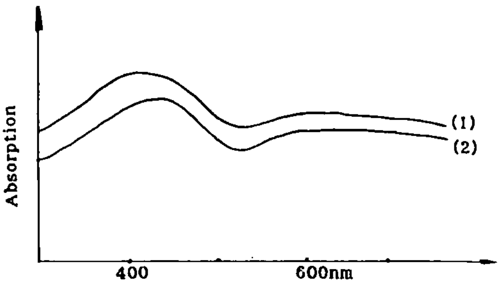

Fig.2: PAS of polymeric[Cu(dien)I_2]$_n$(1) and PAS of monomeric[Cu(dien)I_2](2)

The principal parameters about dien coordinating with Cu ion in the title complex are good in agreement with the monomer,the dien is almost in the same plane,but the angle I(1)-Cu-N(2) (174.0°) is larger than the corresponding angle (148.6°) in the monomer[13],the angle I(2)-Cu-I(2b) (167.7°) less than 180°.The axial Cu-I bond length of 3.348 Å (average) is larger than the Cu-I(2) distance of 3.049 Å in [Cu(dien)I_2] and the terminal Cu-I(1) bond length of 2.585 Å is comparable to the Cu-I(1) distance of 2.619 Å in the monomeric complex.There are few Cu-I distances with which to compare the present results[13],a bond

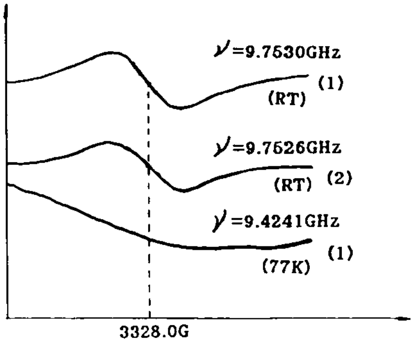

Fig.3: ESR of polymeric$[Cu(dien)I_2]_n$(1) and ESR of monomeric$[Cu(dien)I_2]$(2)

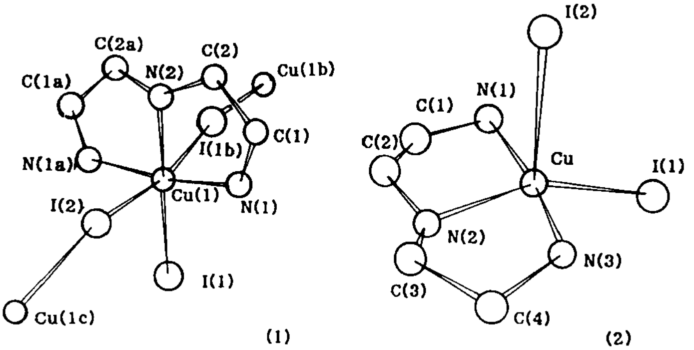

Fig.4: The crystal structure of the title complex(1) and the crystal structure of monomeric $[Cu(dien)I_2]$(2) [13]

length of 2.70 A was reported for $[Cu(bpy)_2I]^+$[13,14].While Barclay et al.[14] regarded this distance as 'normal' since they report the sum of the covalent radii of Cu and I as approximately 2.68 A,Zhdanov[15] gave a smaller value of 2.61 A.Hence,the present Cu-I(2) distance is abnormally long,while the Cu-I(1) separations in both species are similar to that predicted on the basis of Zhdanov's compilation[13].

2:The electronic spectrum

The crystals give an electronic spectrum consisting of a strong broad band thus the d-d transition absorption peaks undistinguished.After resolved by an

Tab.1: The First Coordinate Globe Bond Distances(A) and Angles(deg) in Polymeric$[Cu(dien)I_2]_n$ and Monomeric$[Cu(dien)I_2]$ [13]

(a)Bonds

polymer		monomer	
Cu-I(1)	2.585(1)	Cu-I(1)	2.619(2)
Cu-N(2)	2.030(7)	Cu-N(2)	2.034(9)
Cu-I(2)	3.325(1)	Cu-I(2)	3.049(2)
Cu-N(1)	1.998(5)	Cu-N(1)	1.986(7)
Cu-N(1a)	/	Cu-N(3)	1.999(7)
Cu-I(2b)	3.371(1)		

(b)Angles

polymer		monomer	
I(1)-Cu-N(1)	96.1(2)	I(1)-Cu-N(1)	96.5(3)
N(1)-Cu-N(2)	83.9(2)	N(1)-Cu-N(2)	84.2(3)
N(2)-Cu-N(1a)	83.9(3)	N(2)-Cu-N(3)	84.8(3)
I(2)-Cu-I(1)	96.4(3)	I(1)-Cu-I(2)	109.2(1)
I(2)-Cu-N(1)	90.2(0)	I(2)-Cu-N(1)	87.6(3)
I(1)-Cu-N(2)	174.0(7)	I(1)-Cu-N(2)	148.6(2)
I(2)-Cu-N(1)	90.2(13)	I(2)-Cu-N(1)	87.6(3)
I(2)-Cu-N(2)	89.6(6)	I(2)-Cu-N(2)	102.3(2)
I(2)-Cu-N(1a)	/	I(2)-Cu-N(3)	86.4(3)
I(2)-Cu-I(2b)	167.7(1)		

Tab.2: Crystal Field Parameters of $[Cu(dien)I_2]_n$

Cu		Cu	
μ(Debye)	1.73500	$\langle r^2 \rangle$(a.u.)	2.36234
t	0.05732	$\langle r^4 \rangle$(a.u.)	15.56459
N^2	0.94	$\langle r^{-3} \rangle$(a.u.)	5.39340
$p^{(2)}$	1.60481	B (cm^{-1})	947
$p^{(4)}$	2.14914	C (cm^{-1})	3243
Ω(Hartree)	0.20285	b_{3d} (cm^{-1})	516

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

IBM PC/XT program[16].The d-d spectrum exhibits three absorption peaks at *ca* 11488,14715 and 18025cm^{-1} (Fig.1).These values were alse listed in table.3 as observed ones.

In ligand field theory,Li Jianmin *et al.* had suggested a non-free ions wave function radial scaling theory[17] for which a program package (FLFT)[16] had been developed and the radial wave function of Cu(II) can be written in double b as[18]

Tab.3: The d-d Transition Energy of $[Cu(dien)I_2]_n$

energe order	calc.(cm^{-1})	obs.(cm^{-1})
${}^2A'({}^2T_{2ga},t)$	0	
${}^2A'({}^2E_{ga},e)$	11021 (1)	11488 (1)
${}^2A''({}^2T_{2gb},t)$	14834 (2)	14715 (2)
${}^2A''({}^2E_{gb},e)$	18308 (3)	18025 (3)
${}^2A'({}^2T_{2gc},t)$	20557	

$$R_{3d}(r,\Omega)=C^{-1/2}[0.55428\cdot STO(b_1)+0.60500\cdot STO(b_2)]$$

$$=a1\cdot STO(b_1)+a2\cdot STO(b_2)$$

where,

$$b_1=6.3496(1-0.41500\cdot\Omega+0.25000\cdot\Omega^2),$$

$$b_2=2.5250(1-1.64500\cdot\Omega+0.35500\cdot\Omega^2),$$

C is normalization coefficient,and Ω is so-called scale of nonfreedom,a variable parameter determined by the number of ligands,average bond length, the ratio of dipole length and bond length t,and the average dipole moments of ligands μ,to describe the deviation of central ion from free ion. So far the PLFT have successfully explained spectroscopic properties of more than one hundred transition-metal complex crystals[11,12,19,20].From the crystal structure data the crystal field parameters and relative energy levels can be calculated by PLFT.The values were listed in the table 2 and table 3 as calculated values.

In the table 3,we can find the calculated values are in agreement with the observed ones,thus indicating the electronic structure of the title complex is in accord with its crystal structure.It also indicates a weak spin-exchange interaction operation between the two copper ions[12].In addition,in the fig.1 we can find that the d-d absorption peaks of the title complex are almost the same as the monomeric $[Cu(dien)I_2]$.This also indicates a weak superexchange interaction between the two copper ions.Hence,the theoretical calculation eliminate the action of axial Cu-I bond.The theoretical peak of 20557 cm^{-1} can not be observed because we eliminate the action of axial I ion,so that the ligand field has a higher symmetry and the theoretical "d-d" absorption peak (20557 cm^{-1}) was caused.The title complex absorption near 11000 cm^{-1} is weaker than monomeric [Cu(dien)I_2].This may be the title complex axial coordination is weaker than monomer and it makes the ligand field stronger,so that the whole absorption spectrum have a violet shift (average).

3:PAS

In fig.2,we can find that the absorption peaks of the title complex are almost in agreement with the monomer.There is only a little difference in the region of 400-500nm.The small difference can imply a weaker bridged action, namely a weak spin-exchange interaction ($2J=-3cm^{-1}$)[13].Apparently,the absorption of 400-500nm of the title comlex is mainly caused by charge transition absorption from terminal iodide ion to Cu ion.

In the title complex,I ion has a strong reduction.The intrachain Cu-Cu separation is 6.658(1) A[13].According to Coffman rule[21],this implies Cu(II)-Cu(II) can form a strong spin-exchange interaction *via* the chain-propagating I ions,but the interaction is very weak because of the weak coordination of bridged I ion.

Recently,Kahn has reported to use approximate molecular orbital model to calculate the exchange integral J.According to Kahn's theory[22-25],the S-T energe gap 2J in a binuclear copper(II) complex may be expressed as the sum of a negative antiferromagenetic contribution J_{AF} and a positive ferromagnetic contribution J_F: $2J=J_{AF}+J_F$

J_{AF} varies as the square S^2 of the overlap integral between the magnetic orbitals and J_F as the two-electron-exchange integral between these magnetic orbitals.The latter contribution is likely vanishing because of the weak coordination of the chain-propagating I ions (the bond length are 3.325 and 3.371 A,respectively.)[22-26].In addition,the chain-propagating I ions are in the axis,the two magnetic orbitals ($d_{x^2-y^2}$) is almost parallel and has a distance of 6.658 A,so that they can barely overlap.S and J_{AF} are close to zero. A weak antiferromagnetic property is caused by the spin-exchange interaction.

In fig.2,we can find that the d-d transition absorption peaks are in the high energy region.Absorption edge near 540 nm because of the stronger square coordination and weaker axial coordination.In the corresponding region (300-800nm),the PAS is apparently coincident with the electronic spectrum.

4:ESR

The room temperature powder ESR spectrum for the title complex was given in the fig.3.The spectrum only exhibits a quasi-isotropic feature around g=2.0942. It shows neither fine structure nor a half-field transition,which is characteristic of a pair triplet state. In addition,the spectrum is almost the same as the monomer.These also prove the weak superexchange interaction between the two Cu ions,which is in agreement with the result above.The g value is greater than 2.04,conforming to a ground state configuration with unpaired electron in the $d_{x^2-y^2}$ orbital[27].At 77K,our ESR can't give more information about the title complex.

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