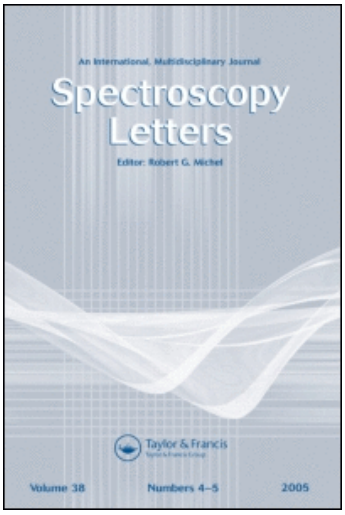

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THE ELECTRONIC ABSORPTION SPECTRA OF BINUCLEAR COMPLEXES, [Cu(o-phen)(sal)]NO3 AND [Cu2(sacch)4(im)4] CRYSTAL

Key words: electronic spectra, complex, ligand field theory

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ABSTRACT

The electronic absorption spectra of crystals of the title compounds were recorded and the experimental results were explained quantitatively with the ligand field theory and the radial wave function of bound Cu(II) cation. With these spectra, the range of magnetic interactions between two Cu(II) ions of the title compounds are discussed.

INTRODUCTION

Recently, some researchers had widely studied a series of complexes with the formula: Cu(II)(N-N)(O-O), where N-N means o-phenanthroline, bipyridine and their derivatives; O-O means salicyladehyde and its derivative[1]. The crystal and molecule structures of these complexes have been determined[2]. But the

study of their other characters was limited. The electronic absorption spectra of complexes' crystals, usually as a basic substance of electronic structure of crystal, have not been reported yet. In this work, electronic absorption spectra of the title compounds are determined and explained for the first time.

As early as in 1983, S.Z.Haider reported a series of transition metal complexes' crystal structures in which saccharin, a compound had some close relations with our life, was used as ligand[3]. In 1989, the complex's crystal of $[Cu_2(sacch)_4(im)_4]$ were synthesized and its crystal structure was also recorded[4]. However, there was something interesting that half of the saccharin molecules provides two coordinating points and this has never been found before. Eager to make out the structural chemistry properties of this complex, we recorded the electronic absorption spectrum of thetitle compound and perfectly explained them with the wave function radial scaling theory[5,6].

In the complexes crystal system of Cu(N-N)(O-O), the coordination group forms a dimer state. Therefore, in $[Cu_2(sacch)_4(im)_4]$ complex, two divalent copper cations linked with two saccharin molecules (there are another two saccharin and four imidazole molecules) form an octagonal ring $(-Cu-O-C-N-)_2$ structure. In this kind of binuclear complexes, for the spin magnetism of divalent copper cations, two central ions will bring out a strong magnetic interaction which takes place within a certain distance. As a result, it makes energy levels of spectral terms take a further split. However, with the electronic absorption spectra of binuclear complexes' crystals, sphere of magnetic interaction between central ions is discussed in ligand field theory.

EXPERIMENT

$[Cu(o\text{-}phen)(sal)]NO_3$:

The mixed-ligand Cu(II) complex was obtained by the reaction among $Cu(NO_3)_2$, salicylaldehydato and o-phenanthroline in an

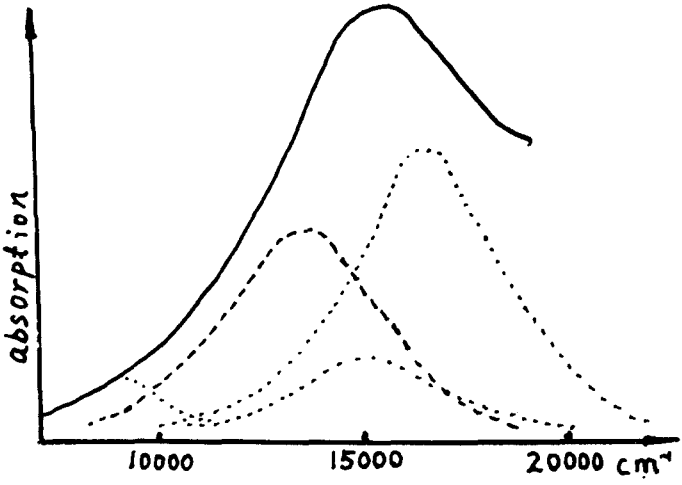

FIG. 1. The electronic absorption spectrum of [Cu(o-phen)(sal)]NO_3 crystal

aqueous-alcohol solution. Dark-green pinacords (0.5×0.4×1 mm^3) crystallites will grow, evaporating slowly at room temperature. The result of elements analysis is C: 53.40, H: 3.05, N: 9.85 and that corresponds with the formula: $CuC_{17}N_3O_5H_{13}$ of the title compound. Therefore, the crystal is in triclinic, space group is P1, and crystallographic data of this crystal is that a=11.739(3), b=9.062(2), c=8.773(2)A, α=95.74(2), β=112.78(2), γ=79.81(1)°. Using the absorption spectrograph for small crystal, the electronic absorption spectrum of the title compound was recorded at room temperature in the region of 5000-30000cm^{-1}, by the Geochemistry Institute of the Academy of Science of China. see Figure 1. In addition, the overlapping electronic absorption bands were resolved by the computer in order to pick out the absorption peaks respectively.

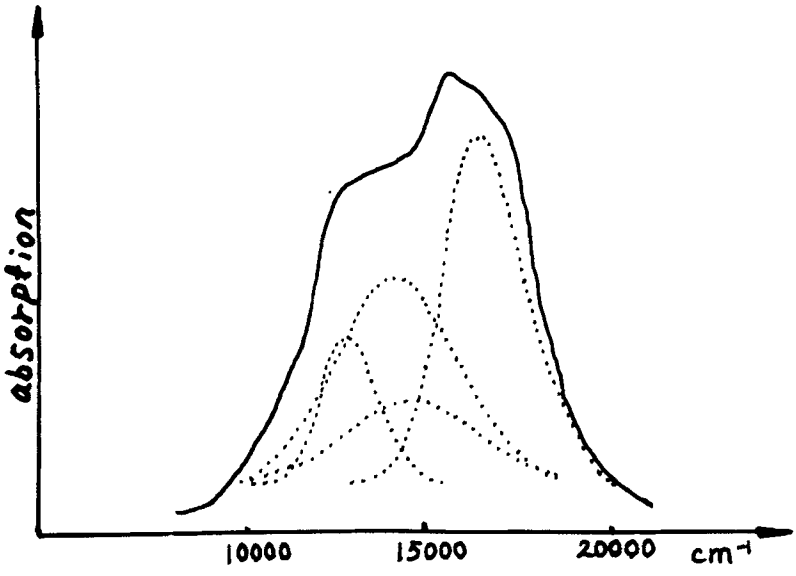

FIG. 2. The electronic absorption spectrum of [Cu2(sacch)4(im)4] crystal

[Cu2(sacch)4(im)4]:

The compound was obtained by the reaction between imidazole and Cu(sacch)2(H2O)4[3] in the molar ratio 2:1 in aqueous solution. The mixture solution was heated in a water bath at 80-90°C with continuous stirring. Blue crystals grew and repeated crystallizing from water at room temperature. The results of elements analysis and IR spectrum were in accordance with its structure formula: Cu2(C6H4COSO2N)4(C3H4N2)4. In the same conditions, the electronic absorption spectrum of the title compound was determined. The overlapping absorption bands were also resolved by computer, see Figure 2.

RESULTS AND DISCUSSION

In ligand field theory, Li Jianmin et al. had suggested a non-free ions wave function radial scaling theory and developed a program package for the calculation of this ligand field theory(PLFT)[7]. The crystal field parameters, electronic absorption spectra and ESR spectra of hundreds kinds of complexes crystals have been calculated theoretically by the PLFT. However, good results from calculation are almost in perfect agreement with the experimental values. The errors of the absorption position in electronic spectra are always less than 5 percent[8,9]. In these two complexes system, the non-free radial wave function of Cu^{2+} ion is that:

$$R(r,\Omega) = C^{-1/2}[\ 0.55428\ STO(\zeta_1) + 0.605\ STO(\zeta_2)\ ]$$
$$\zeta_1 = 6.3496\ (\ 1 - 0.415\ \Omega + 0.250\ \Omega^2\ )$$
$$\zeta_2 = 2.5250\ (\ 1 - 1.645\ \Omega + 0.355\ \Omega^2\ )$$
$$C = 1 - 0.67078\ \{\ 0.48719 - [\ 2\ (\zeta_1\zeta_2)^{1/2}/(\zeta_1 + \zeta_2)]^7\}$$

where, C is a renomalization coefficient when it is transfered to non-free environment and Ω is called the scale of non-freedom, which is a variable parameter to describe the deviation from free ion.

The d-d Transition Energy Levels Of [Cu(o-phen)(sal)]NO3

According to the crystal structure data of the title compound[1], the divalent copper cation in this ternary complexes displays a distorted square-pyramidal coordinating structure. It directly coordinates with two oxygen atoms of salicylaldehydato and two nitrogen atoms of o-phen and one oxygen atom originated from nitrogen group. However, because of the dimer coordination structure, there exists a very weak interaction between Cu^{2+} cation and oxygen atom from another salicylaldehydato molecule. see Figure 3. In this complex, the coordination lattice takes Cs symmetry and the crystal structure data are given in Table 1.

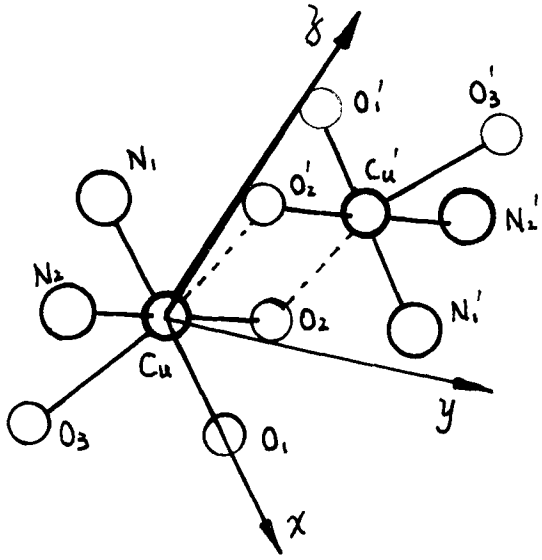

FIG. 3. The coordinated structure of the [Cu(o-phen)(sal)]NO3 crystal

TABLE 1

The Crystal Structure Data of The Title Compounds

[Cu(o-phen)(sal)]NO3				[Cu2(sacch)4(im)4]			
atom	R(A)	θ(deg.)	Φ(deg.)	atom	R(A)	θ(deg.)	Φ(deg.)
O1	1.952	90.0	0.0	O4	2.266	90.0	0.0
O2	1.898	88.0	93.6	N1	2.069	90.0	238.7
O3	2.402	30.0	220.0	N2'	2.113	90.0	105.6
N1	2.005	90.0	173.8	N3	1.958	176.9	55.0
N2	1.991	92.0	268.1	N5	1.948	5.0	285.0
O2'	2.781	8.0	45.0				

TABLE 2

The Crystal Field Parameters of The Title Compounds

	[Cu(o-phen)(sal)]NO3	[Cu2(sacch)4(im)4]
μ(debye)	1.10133	1.19560
t	0.03775	0.05572
N^2	0.9100	0.9980
Ω(hartree)	0.20293	0.16987
ζ1	5.74949	5.85616
ζ2	1.71902	1.84527
a1	0.59280	0.58594
a2	0.64704	0.63956
B (cm^{-1})	950.0	1012.0
C (cm^{-1})	3379.0	3610.0
ζ3d(cm^{-1})	516.0	553.0

TABLE 3

The d-d Transition Energy Levels of The Title Compounds

energy levels	[Cu(o-phen)(sal)]NO3		[Cu2(sacch)4(im)4]	
	cal.	obvs.	cal.	obvs.
^{2}Egb (^{2}Eg ,e)	0.	0.	0.	0.
^{2}T2gc(^{2}T2g,t)	10994.	9100.	12180.	12660.
^{2}Ega (^{2}Eg ,e)	13283.	13200.	14102.	14100.
^{2}T2ga(^{2}T2g,t)	16281.	15100.	15092.	14750.
^{2}T2gb(^{2}T2g,t)	16380.	16200.	15876.	16320.

With the data in Table 1, the crystal parameters and d-d transition energy levels of the title compound are calculated. However, in the course of calculation, there is only one variable parameter that is N^2 called covalent factor (see Table 2.) to describe the degree of covalence in coordination bonds.

The results of calculation are shown in Table 2 and 3. Therefore, there exist four absorption peaks at the position of 9100, 13200, 15100, and 16200 cm^{-1}.

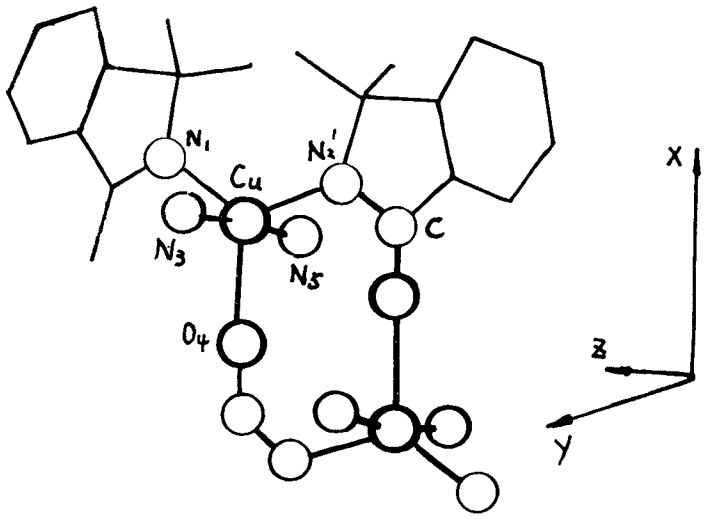

FIG. 4. THe coordinated structure of the [Cu2(sacch)4(im)4] crystal

The d-d Transition Energy Levels Of [Cu2(sacch)4(im)4]

The [Cu2(sacch)4(im)4] crystal structure is composed of two symmetric Cu^{2+} coordination group. On the other hand, coordinations between two divalent copper cations and two saccharin molecules (each one provides two chelate points) form an octagonal ring (-Cu-O-C-N-)2, see Figure 4. The distance between two Cu^{2+} cation is nearly 4.5A, In each Cu^{2+} coordination group, Cu^{2+} cation linked with three saccharin and two imidazole molecules and forms five coordination bonds and trigonal--bipyramidal stereochemistry. The coordinate system is assigned as shown in Figure 4. The coordination lattices takes Cs symmetry.

With the structural data in Table 1, the crystal field parameters and the d-d transition energy levels of [Cu2(sacch)4(im)4] crystal are calculated by PLFT. The results are listed in Table 2 and 3. However, the experimental values are perfectly corresponding with the calculated ones.

The Effect Of The Magnetic Interaction Between Divalent Copper cations

From the results of [Cu(o-phen)(sal)]NO_3 in Table 3, we see there are some large errors between the values of calculation and experiment. Therefore, as the transition of $^2Egb \rightarrow {}^2T_2gc$, the calculation results is 10994 cm^{-1} and that of observed is 9100cm^{-1}. The unsatisfactory error of this transition is about 20%. And that of the transition $^2Egb \rightarrow {}^2T_2ga$ is also nearly 8%. However, there are something much large than the theoretical system's error. And this unsatisfactory result has never occurred before when we discussed those other complexes. Comparably, from Table 3, we find the observational values of $[Cu_2(sacch)_4(im)_4]$ crystal correspond well with the calculated ones.

For the single d electron, some transition metal ions have spin magnetism. In single nuclear complexes, the effect of electron exchange interaction is something very little and may be ignored. But in binuclear complexes, there is a strong magnetic interaction that will apparently effect the complexes' crystal potential energy field. It will partly decide the characterization of these complexes. In divalent copper cations complexes, there are always some paramagnetism because of the spin magnetism of Cu^{2+} cations. So, when it forms binuclear complexes, this magnetism interaction between two divalent copper cations will cause the energy levels in ligand field make some further split and bring about some new errors. However, in the dimer complexes' crystal, the distance between two Cu^{2+} cations is 3.486A. There is a strong magnetic interaction between them and that is why we get an irregular result with those large errors. But, in the dimer complexes $[Cu_2(sacch)_4(im)_4]$ crystal, we obtained good results with a regular error. From the octagonal ring structure, we know that the distance between two Cu^{2+} cations is nearly 4.5A. In this range, the magnetic interaction is very weak. So the affection of this magnetic interaction to the potential energy field is also very weak and negligible. From all this, we come to this conclusion, in binuclear divalent copper ion complexes, when the

distance between two Cu^{2+} cations is shorter than 3.5A, there will have a strong magnetic interaction and it will be evidently shown in crystal electronic absorption spectra. But, if the distance is large than 4.5A, the magnetic interaction will be much weak and it's affection may be negligible.

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