EPR Studies of Cu^{2+} Doped Zinc Saccharin, $[Zn(sac)_2{\cdot}(H_2O)_4]{\cdot}2H_2O$ Single Crystals

İ. Kartal, B. Karabulut, F. Köksal, and H. İçbudak[a]
Department of Physics, Faculty of Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey [a]
Department of Chemistry, Faculty of Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey
Reprint requests to Dr. İ. K.; E-mail: ikartal@omu.edu.tr

Z. Naturforsch. **55 a,** 887–890 (2000); received October 13, 2000

The EPR spectra of Cu^{2+} in zinc saccharin crystalline powder and single crystals have been recorded at room temperature. The angular variation of the spectra indicates the substitution of the host Zn^{2+} with Cu^{2+}. Two magnetically inequivalent sites for Cu^{2+} have been observed. The spectra were fitted with a rhombic spin-Hamiltonian, and the ground state wave function of the complex has been constructed.

Key words: EPR; Zinc Saccharin; Cu^{2+}; Ground State Wave Function.

Introduction

It was of interest for many scientists to study transition metal ions as probes in different symmetry environments by electron paramagnetic resonance technique (EPR). Using the paramagnetic ion as an impurity probe, one could study the behaviour of paramagnetic ions and estimate the site symmetry of the ion present in the lattice [1 - 5]. In most of the Cu^{2+} doped compounds, the Cu^{2+} ions replace divalent cations. Saccharin (sac) is extensively used as a non-caloric sweeting agent [6], and forms $[M(sac)_2{\cdot}(H_2O)_4]{\cdot}2H_2O$ complexes, where M is a divalent metal ion, such as Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} [7]. Single crystal X-ray analyses of these complexes reveal that they are isostructural and crystallize in the monoclinic space group $P2_1/c$ [7]. All the metal ions have octahedral geometry, surrounded by four water molecules and two saccharinate anions, $(C_7H_4NO_3S)^-$, by breaking a N-H bond, in the trans positions. The remaining two water molecules are present as lattice water. The thermal decomposition of these complexes was studied, and a solid-state phase transition was observed at 227 °C for the Zn complexes [8]. We have not seen any EPR study of these complexes in the literature.

In this paper, the results of a detailed investigation of the **g** and the hyperfine interactions (**A**) in Cu^{2+} doped $[Zn(sac)_2{\cdot}(H_2O)_4]{\cdot}2H_2O$, zinc saccharin (hereafter) using EPR technique are reported. The EPR spectra of Cu^{2+} in zinc saccharin single crystal and powder at room temperature are given, and the ground state wave function of the Cu^{2+} ion is constructed [5, 9 - 12].

Experimental

Single crystals of Cu^{2+} doped zinc saccharin were grown by slow evaporation of saturated aqueous solutions admixtured in stochiometric ratios with about 0.05% $CuCl_2$. Well-developed single crystals of suitable size were selected for the investigation after about a week. The single crystals were mounted on a goniometer, and the EPR spectra were recorded when the magnetic field is in three mutually perpendicular planes (a^*c, a^*b, bc) by rotating the magnetic field at 10° intervals at room temperature. Here a^* is perpendicular to crystallographic b and c axes. The EPR spectrum of a powder sample was also recorded at room temperature. The spectra were recorded with a Varian E-109C model X-band EPR spectrometer. The magnetic field modulation frequency was 100 kHz, and the **g** values were found by comparison with a diphenylpicrylhdrazyl sample of $g = 2.0036$.

Results and Discussion

The EPR spectra of Cu^{2+} doped zinc saccharin taken at all orientations of the magnetic field at room temperature show two sets of four hyperfine lines,

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Table 1. Spin-Hamiltonian parameters of Cu^{2+} doped zinc saccharin. $\Delta g = \pm 0.002$, $\Delta A = \pm$ 0.2 mT.

		Direction cosines			Hyperfine		Direction cosines	
Site	**g**	a^*	b	c	**A** (mT)	a^*	b	c
I	$g_{xx} = 2.140$	0.658	±0.317	0.683	$A_{xx} = 2.01$	–0.815	±0.110	0.569
	$g_{yy} = 2.053$	0.706	±0.056	–0.706	$A_{yy} = 4.63$	0.542	±0.202	0.816
	$g_{zz} = 2.384$	0.262	±0.947	0.187	$A_{xx} = 11.4$	0.202	±0.973	0.105
II	$g_{xx} = 2.127$	–0.814	±0.110	0.569	$A_{xx} = 2.73$	0.959	±0.246	0.139
	$g_{yy} = 2.045$	0.542	±0.202	0.816	$A_{yy} = 4.38$	0.104	±0.149	0.983
	$g_{zz} = 2.386$	0.205	±0.973	0.105	$A_{xx} = 11.32$	–0.262	±0.958	0.117

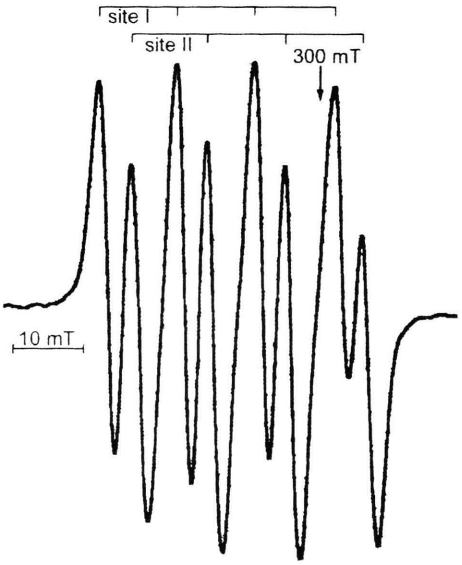

Fig. 1. EPR spectrum of Cu^{2+} doped in zinc saccharin when B is in the a^*b plane and makes 80° with the b axis.

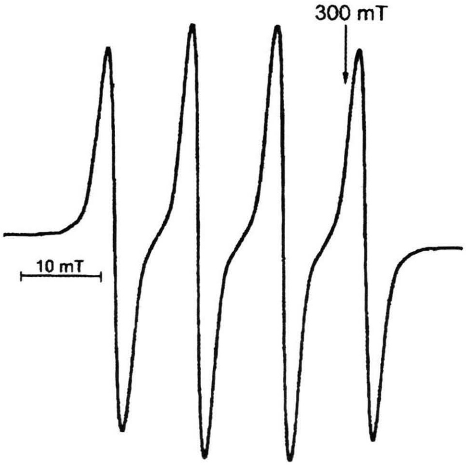

Fig. 2. EPR spectrum recorded when the magnetic field is along the a^* direction.

which come from two magneticaly inequivalent sites. Since the lines are relatively broad, the ^{63}Cu and ^{65}Cu hyperfine lines are not clearly resolvable at all orientations as seen in Figs. 1 and 2. Figure 1 shows the EPR spectrum of Cu^{2+} recorded when the magnetic field is 80° away from the b axis. This spectrum consists of two sets of four hyperfine lines due to the interaction of the unpaired electron ($S = 1/2$) with the copper nucleus ($I = 3/2$). Another distinguished EPR spectrum is recorded when the magnetic field is along the a^* axis, as shown in Figure 2. This figure displays obviously only a set of EPR lines for the Cu^{2+} ions.The angular variations of the EPR spectra of Cu^{2+} doped zinc saccharin single crystals are shown in Figure 3. For single crystals, when the magnetic field is along the crystallographic b-axis or in the a^*c plane, the spectra consist of a single set of four hyperfine lines, but when the magnetic field is in the a^*b and bc planes, the spectra consist of two sets of four hyperfine lines of the Cu^{2+} ions. This behaviour is consistent with the monoclinic symmetry of the crystals. The whole spectra were fitted with a rhombic spin-Hamiltonian [13]

$$\mathcal{H} = \beta(g_{xx}B_xS_x + g_{yy}B_yS_y + g_{zz}B_zS_z) \quad (1)$$
$$+ A_{zz}B_zS_z + A_{xx}B_xS_x + A_{yy}B_yS_y.$$

The principle values of the **g** and **A** tensors and their direction cosines were found by a diagonalization procedure, the results being given in Table 1 [14]. From these results it is inferred that there are magnetically inequivalent but chemically equivalent two Cu^{2+} ions in the unit cells of the zinc saccharin single crystals. These results are consistent with the monoclinic symmetry properties, and it is concluded that Cu^{2+} substitutes Zn^{2+} ions. From the EPR parameters, which are shown in Table 1, we deduce that Cu^{2+} ions have an octahedral environment with a rhombic distortion.

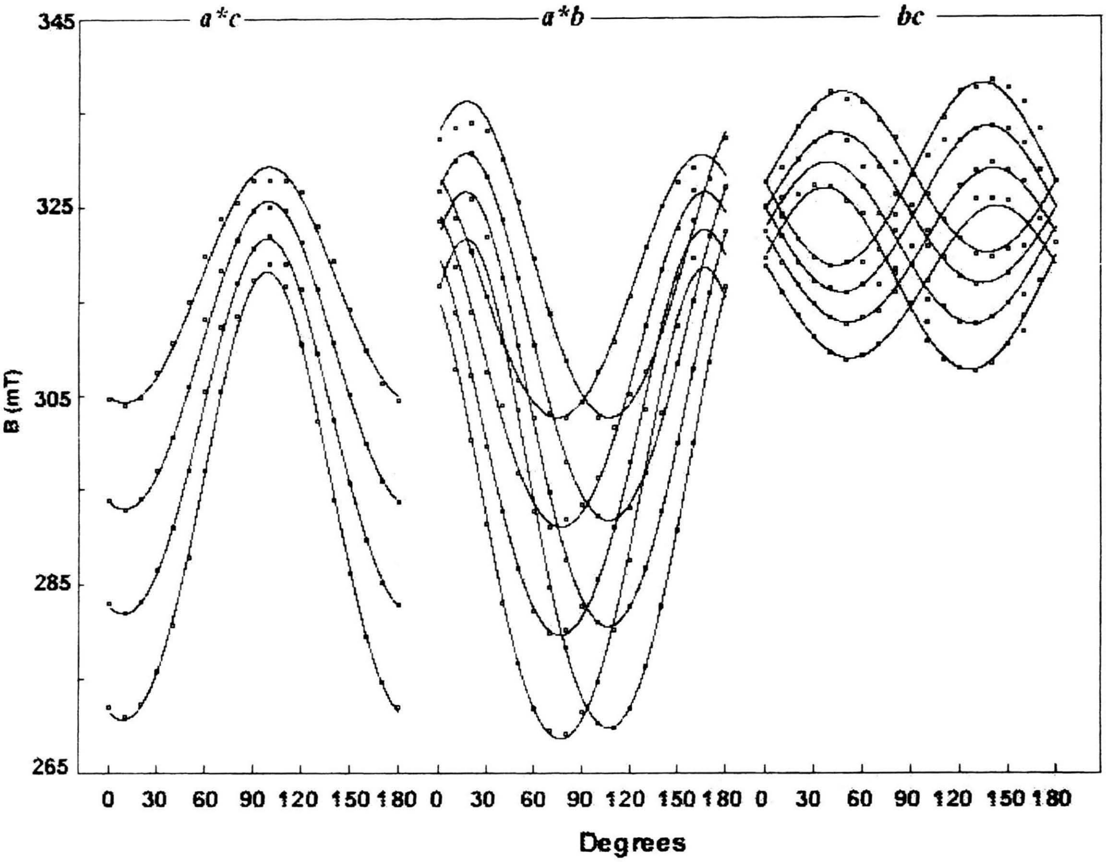

Fig. 3. Angular variations of the EPR spectra of Cu^{2+} doped zinc saccharin single crystals.

The EPR spectrum of the crystalline powder, depicted in Fig. 4, shows clearly that the symmetry of the complex in the crystal is not axial. The powder EPR spectrum was partially resolved into three components. These are consistent with the results for the single crystals in Table 1. The measured values are g_{xx} = 2.126, g_{yy} = 2.051, g_{zz} = 2.374; A_{xx} = 2.4 mT, A_{yy} = 4.0 mT and A_{zz} = 10.93 mT.

The d orbitals of a d ion split into a doublet of E_g and a triplet of T_{2g} symmetry states in an octahedral crystal field. The base functions of E_g, are $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, and the degeneracy of the energy levels are removed in a distorted crystal field. When the site symmetry is tetragonal, the ground state is either $d_{3z^2-r^2}$ or $d_{x^2-y^2}$ depending on whether the distortion is compressional or elongational [9]. When the site symmetry is rhombic or lower, then the ground state is an admixture of these d orbitals. So, the ground state wave function of Cu^{2+} can be written as

$$\psi = \alpha'[\alpha|x^2 - y^2\rangle + \beta|3z^2 - r^2\rangle], \tag{2}$$

where the square of α' is the probability of finding the electron in the metal d orbitals [9, 10, 15 - 17]. The normalization condition for the mixing coefficients α and β is

$$\alpha^2 + \beta^2 = 1. \tag{3}$$

The ground state wave function parameters of Cu^{2+} ions observed in different environments are listed in Table 2. All the calculations were made by using a simple computer program based on Bhaskar Rao and Narayana expressions [9]. The ground state wave functions of the sites by using Table 2 are found to be

$$\psi = (0.900)^{1/2}[0.987|x^2-y^2\rangle+0.163|3z^2-r^2\rangle], \tag{4}$$

$$\psi = (0.892)^{1/2}[0.986|x^2-y^2\rangle+0.169|3z^2-r^2\rangle]. \tag{5}$$

Table 2. Ground state wave function parameters of Cu^{2+} ions, observed in different environments. κ is the Fermi-contact term, for α', α, and β see (2).

Enviroment	Temp.	Site	κ	α'^2	α	β	δg_{exp}	δg_{cal}	Ref.
$[Zn(sac)_2\cdot(H_2O)_4]\cdot 2H_2O$	300 K	I	0.317	0.900	0.987	0.163	0.087	0.100	This
		II	0.322	0.892	0.986	0.169	0.082	0.091	work
$Cd(NH_4)_2(SO_4)_2\cdot 6H_2O$	113 K		0.365	0.866	0.982	0.190	0.080	0.113	[11]
dl-Aspartic acid	300 K	I	0.137	0.868	0.994	0.111	0.041	0.052	[5]
		II	0.136	0.814	0.992	0.125	0.057	0.036	
$Na_2Zn(SO_4)_2\cdot 4H_2O$	30 K		0.21	0.99	0.310	0.940	0.253	0.263	[9]
$K_2Zn(SO_4)_2\cdot 6H_2O$	20 K		0.28	0.90	0.977	0.213	0.117	0.118	[9]
$Rb_2Zn(SO_4)_2\cdot 6D_2O$	20 K		0.29	0.95	0.981	0.194	0.110	0.114	[9]
$K_2Zn(ZrF_6)_2\cdot 6H_2O$	4.2 K		0.38	0.84	0.990	0.118	0.066	0.065	[9]
$CdK_2(SO_4)_2\cdot 6H_2O$	77 K		0.315	0.769	0.996	0.077	0.07	0.084	[10]

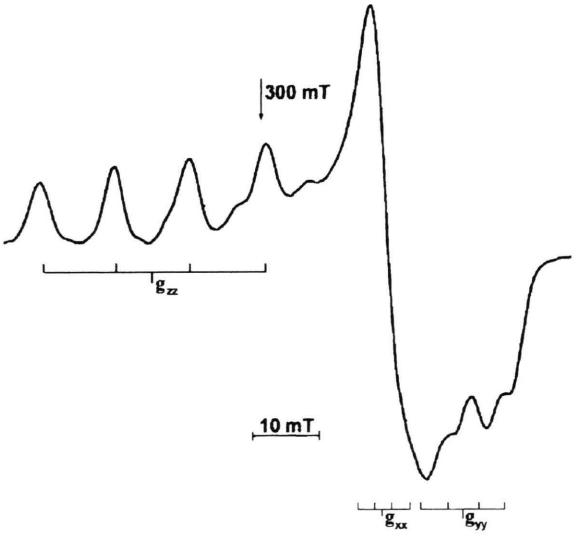

Fig. 4. Powder EPR spectrum of Cu^{2+} doped zinc saccharin.

From these results, the covalency parameter, $\alpha'^2 = 0.900$, obviously explains that the unpaired electron spends 10% of its time on ligand orbitals, whereas the rest is spent on the Cu^{2+} d orbitals for the site I. Since the coefficient of $d_{x^2-y^2}$ is significantly grater than that of $d_{3z^2-r^2}$, one can conclude that the rhombic distortion results dominantly from the $d_{3z^2-r^2}$ orbital of the Cu^{2+} ion.

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