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# EPR spectra of Cu<sup>2+</sup> doped [Zn(sac)<sub>2</sub>(dmen)] and [Zn(sac)<sub>2</sub>(paen)] single crystals

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## Abstract

 $Cu^{2+}$  doped single crystals of [Zn(sac)<sub>2</sub>(dmen)] (sac: saccharinate, dmen: *N*,*N*'-dimethylethylendiamine) and [Zn(sac)<sub>2</sub>(paen)], (paen: *N*,*N*'-bis(3-propylamine)ethylendiamine) complexes have been investigated by electron paramagnetic resonance (EPR) technique. Detailed investigations of the EPR spectra indicate that  $Cu^{2+}$  ion substitute with Zn<sup>2+</sup> ion and forms tetrahedral complex in [Zn(sac)<sub>2</sub>(dmen)] and octahedral complex in [Zn(sac)<sub>2</sub>(paen)] hosts. Principal values of the *g* and hyperfine tensors are determined and the ground state wave functions of  $Cu^{2+}$  ions are obtained using EPR parameters.

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### 1. Introduction

Studies on paramagnetic transition metal ion complexes in diamagnetic host lattices are reported by many authors and structural properties are discussed [1-11]. When the transition metal ions are doped in a diamagnetic host lattice as an impurity, they form paramagnetic centers from which the structures of the local symmetry can be obtained by means of electron paramagnetic resonance (EPR) spectroscopy, which is one the most efficient techniques to get information about the structure, symmetry, the effects of environmental structures and electric field in complexes. These ions mostly replace a divalent or monovalent cation in the host by compensating the charge deficiency with some other nuclei in the host.

Due to their importance in biological applications saccharine, its derivatives and their metal complexes are being studied widely. Various water soluble alkaline salts of saccharine are used as low or non caloric synthetic sweeteners and as antidotes against metal poisoning [12–14]. General formula of metal complexes of saccharine is [M(sac)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O, where M is a divalent metal ion such as  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$ .

1386-1425/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2006.12.008 In this study, two newly synthesized saccharinate complexes  $[Zn(sac)_2(dmen)]$  and  $[Zn(sac)_2(paen)]$ , are studied with EPR spectroscopy by doping paramagnetic Cu<sup>2+</sup> ion to substitute for  $Zn^{2+}$  in the host to see how the complex is formed.

#### 2. Experimental

Water solution of dmen (0.176 g, 2.0 mmol) and paen (0.350 g, 2.0 mmol) are added drop wise into separate 50 mL water solution of  $[\text{Zn}(\text{sac})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$  [11] (0.548 g, 1.0 mmol) while stirring continuously at room temperature. The solutions, then, are heated up to 80 °C in a temperature controlled bath and stirred continuously for 4 h. The reaction products are cooled to room temperature slowly. Small crystals grown in the solution are filtered out and washed in cold distilled water and ethanol, and dried.

# 2.1. $Cu^{2+}$ doped [Zn(sac)<sub>2</sub>(dmen)] and [Zn(sac)<sub>2</sub>(paen)]

[Zn(sac)<sub>2</sub>(dmen)] and [Zn(sac)<sub>2</sub>(paen)] crystals obtained in previous process are dissolved in 25 mL (1.0 mmol) of hot water kept at 60 °C in temperature controlled heat bath. Approximately 0.1% of CuSO<sub>4</sub> is added to the solution to substitute some Zn<sup>2+</sup> with Cu<sup>2+</sup> ions. The solution then cooled very slowly to room temperature for purification and also for the development of

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Fig. 1. The structures of the complexes (a)  $[Zn(sac)_2(dmen)]$  and (b)  $[Zn(sac)_2(paen)]$  determined with X-ray crystallography.

well shaped single crystals. The crystals grown in the solution are filtered out.

X-ray diffraction analysis of  $[Zn(sac)_2(dmen)]$  single crystals shows that crystal symmetry is monoclinic with unit cell parameters: a=8.512, b=12.34 and c=20.69 Å;  $\beta=101^{\circ}$  and Z=4. With the same analysis made on  $[Zn(sac)_2(paen)]$  crystal, the symmetry is found to be orthorhombic with unit cell parameters: a=10.10, b=14.30, c=19.25 Å and Z=4. The structures of the complexes determined by X-ray diffraction technique are given in Fig. 1.

EPR spectra are recorded with Varian E-109 X-band EPR spectrometer using 100 kHz magnetic field modulation. The single crystals are glued on a quartz rod of a goniometer graded in degrees and rotated at 5° or 10° intervals depending on the variation of spectra in three mutually perpendicular planes. The spectrometer frequency is corrected using the dpph sample (g = 2.0036). Simulations of powder spectra of both compounds were made using Bruker's WINEPR software.

#### 3. Results and discussion

EPR spectra of Cu<sup>2+</sup> doped [Zn(sac)<sub>2</sub>(dmen)] and [Zn(sac)<sub>2</sub>(paen)] single crystals are taken at room temperature for rotations in three mutually perpendicular planes between 0° and 180°. Fig. 2a and b shows the EPR spectra of Cu<sup>2+</sup> doped [Zn(sac)<sub>2</sub>(dmen)] single crystal in  $c^*a$  plane when magnetic field inclined by 45° to the *a*-axis and parallel to *b*-axis, respectively. Fig. 3 shows the spectrum of [Zn(sac)<sub>2</sub>(paen)] single crystal in the *ab* plane with the magnetic field inclined by 140° to the *b*axis. The spectra arise obviously from paramagnetic Cu<sup>2+</sup> ion with nuclear spin of I=3/2.

There are two sets of four lines in all spectra as seen in the plots of angular variation of line position, shown in Figs. 4 and 6. The spectra are resolved by fitting each line to the expression:

$$g_k^2(\theta) = g_{ii}^2 \cos^2 \theta + g_{jj}^2 \sin^2 \theta + 2g_{ij}^2 \sin \theta \cos \theta \tag{1}$$

where *i*, *j* and *k* stand for *x*-, *y*- and *z*-axis, respectively. The coefficients,  $g_{ii}^2$ ,  $g_{jj}^2$  and  $g_{ij}^2$  for each line are used to group the lines belonging to paramagnetic centers and then, to determine the *g* and hyperfine tensors. The tensors formed in this way are diagonalized and principal values obtained.



Fig. 2. EPR spectra of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(dmen)] single crystal (a) in  $c^*a$  plane when magnetic field makes  $45^\circ$  from *a*-axis and (b) magnetic field is along *b*-axis.

The spectra can be fitted to and described by means of the rhombic spin Hamiltonian:

$$\mathcal{H} = \beta_{e}(g_{x}H_{x}S_{x} + g_{y}H_{y}S_{y} + g_{z}H_{z}S_{z})$$
$$+I_{x}A_{x}S_{x} + I_{y}A_{y}S_{y} + I_{z}A_{z}S_{z}$$
(2)

which includes only electron Zeeman and hyperfine interactions. The nuclear Zeeman, spin-orbit and nuclear quadrupole interactions are neglected [14]. In fact, these last interactions are intrinsic in g and hyperfine variations.



Fig. 3. EPR spectra of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(paen)] when magnetic field makes 140° from *b*-axis in *ab* plane.



Fig. 4. Variation of the  $g^2$  values of all lines in three planes of Cu<sup>2+</sup> doped [Zn(sac)<sub>2</sub>(dmen)] single crystal.

# 3.1. $Cu^{2+}$ in $[Zn(sac)_2(dmen)]$

Angular variations of lines of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(dmen)] single crystal taken in three mutually perpendicular planes, shown in Fig. 4, indicate the existence of two  $Cu^{2+}$  sites. The lines of two sites are separable in *ab* and *bc*<sup>\*</sup> planes. The lines of these two sites, however, coincide in  $c^*a$  plane, which is consistent with monoclinic symmetry. The principal *g* and hyperfine values are given in Table 1. The parameters are seen to be rhombic rather then being axially symmetric.

Powder spectrum of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(dmen)] is given in Fig. 5 together with simulated spectrum obtained with experimental spin Hamiltonian values given in Table 1. The *g* and hyperfine values obtained from the powder spectrum are also given in the same table.

<sup>63</sup>Cu<sup>2+</sup> and <sup>65</sup>Cu<sup>2+</sup> lines are not resolvable because of broad line widths. Combining the results given in Table 1 with the Xray crystallographic structure given in Fig. 1, it can be concluded



Fig. 5. Powder spectrum (a) and simulated spectrum and (b) of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(dmen)]. *x* and *y* compenents are not resolvable because of two components are close to each other.

that  $Cu^{2+}$  ion substitutes with  $Zn^{2+}$  ion in the host lattice in pseudotetrahedral ( $D_{2d}$ ) environment [3,5]. The ground state wave functions, assuming hybridization of *s*, *p* and d orbitals of  $Cu^{2+}$  ion in  $D_{2d}$  symmetry are written to second order approximation to be [3,15]:

$$\psi(B_{1}) = \left| \mathbf{d}_{x^{2}-y^{2}} \right\rangle$$
  

$$\psi(B_{2}) = \alpha \left| \mathbf{d}_{xy} \right\rangle + \eta \left| p_{z} \right\rangle$$
  

$$\psi(E) = \gamma \left| \mathbf{d}_{xz}, \mathbf{d}_{yz} \right\rangle + \xi \left| p_{x}, p_{y} \right\rangle$$
  

$$\psi(A_{1}) = \delta \left| \mathbf{d}_{z^{2}} \right\rangle + \delta_{1} \left| s \right\rangle$$
(3)

where  $\alpha$ ,  $\delta$ ,  $\gamma$ ,  $\eta$  and  $\xi$  are the coefficients of related orbitals. The relations between spin Hamiltonian and crystal field parameters are also taken to second order approximation as:

$$g_{||}(=g_{zz}) = g_{e} - \frac{8\alpha^{2}\lambda_{d}}{E_{1}}$$

$$g_{\perp} (=g_{xx} = g_{yy}) = g_{e} - \frac{2(\alpha^{2}\gamma^{2}\lambda_{d} - \alpha\gamma\xi^{2}\lambda_{p})}{E_{2}}$$

$$A_{||}(=A_{zz}) = P_{d} \left[ -\kappa\alpha^{2} + (g_{||} - 2) - \frac{4}{7}\alpha^{2} + \frac{3}{7}(g_{\perp} - 2) \right] + P_{p}\eta^{2} \left(\frac{4}{5} - \kappa\right)$$

$$A_{\perp}(=A_{xx} = A_{yy}) = P_{d} \left[ -\kappa\alpha^{2} + \frac{11}{14}(g_{\perp} - 2) + \frac{2}{7}\alpha^{2} \right] + P_{p}\eta^{2} \left(-\frac{2}{5} - \kappa\right)$$
(4)

where  $\lambda_d = -829 \text{ cm}^{-1}$  and  $\lambda_p = -925 \text{ cm}^{-1}$  are spinorbit interaction constants and  $P_d = 360 \times 10^{-4} \text{ cm}^{-1}$  and  $P_p = 402 \times 10^{-4} \text{ cm}^{-1}$  are dipolar hyperfine parameters for 3d and 4p orbitals of Cu<sup>2+</sup>, respectively.  $\kappa = 0.43$  is Fermi contact parameter [3,17];  $E_1$  and  $E_2$  are the transition energies between  $B_2 \rightarrow B_1$  and  $B_2 \rightarrow E$  states, respectively in  $D_{2d}$  symmetry.

When Table 1 values are used in  $A_{||}$  and  $A_{\perp}$  expressions of Eq. (4), the coefficient  $\eta^2$  is obtained negligibly small compared to  $\alpha^2 \approx 0.4$ . With the obtained value of  $\alpha^2$ , expression for  $g_{||}$  gives  $E_1 \approx 10,800 \text{ cm}^{-1}$  as expected. Similarly  $g_{\perp}$  expression gives  $E_2 \approx 13,000 \text{ cm}^{-1}$  which is in the same order as the values given in previous works provided that  $\gamma^2 \approx 1$  and  $\xi^2 \approx 0$  [3,5]. The coefficients  $\delta$  and  $\delta_1$  are negligibly small higher order contributions. This is the case encountered mostly when the spin-orbit interaction is small compared to ligand field [3]. The results show that hybridization of 4p orbitals are too small to be

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Complex	Site	g	Direction cosiness			A (mT)	Direction cosiness			
			a	b	<i>c</i> *		a	b	<i>c</i> *	
[Zn(sac) <sub>2</sub> (dmen)]	Ι	$g_{xx} = 2.129$	0.965	-0.144	0.218	$A_{xx} = 4.75$	-0.181	0.573	0.798	
		$g_{yy} = 2.028$	0.254	0.706	-0.660	$A_{yy} = 2.17$	0.135	0.819	-0.557	
		$g_{zz} = 2.259$	-0.058	0.692	0.718	$A_{zz} = 17.37$	0.974	-0.006	0.226	
	П	$g_{xx} = 2.114$	0.995	-0.076	0.049	$A_{xx} = 5.00$	0.995	-0.076	0.049	
		$g_{yy} = 2.028$	0.022	0.727	0.685	$A_{yy} = 3.02$	0.022	0.727	0.685	
		$g_{zz} = 2.248$	-0.088	-0.681	0.726	$A_{zz} = 17.37$	-0.088	-0.681	0.726	
Powder spectrum values	$g_{xx} \approx g_y$	$y_y = 2.082, g_{zz} = 2.2$	55, $A_{xx} \approx A_{yy} =$	$3.21, A_{zz} = 17.$	85					
Complex	Site	g	g Direction cosiness			<i>A</i> (mT)	Direction cosiness			
			a	b	с		a	b	с	
[Zn(sac) <sub>2</sub> (paen)]	Ι	$g_{xx} = 2.130$	0.318	-0.470	-0.823	$A_{xx} = 5.4$	0.241	0.743	-0.623	
		$g_{yy} = 2.054$	-0.143	0.834	-0.532	$A_{yy} = 3.1$	-0.154	0.663	0.731	
		$g_{zz} = 2.405$	0.937	0.287	0.198	$A_{zz} = 11.4$	0.958	-0.080	0.274	
	II	$g_{xx} = 2.135$	-0.043	0.651	-0.757	$A_{xx} = 4.9$	0.160	0.870	0.465	
		$g_{yy} = 2.052$	0.234	0.743	0.626	$A_{yy} = 3.5$	0.089	0.456	-0.885	
		$g_{zz} = 2.387$	-0.971	0.150	0.184	$A_{zz} = 11.2$	-0.983	0.183	-0.004	
Powder spectrum values	$g_{xx} = 2.$	$g_{xx} = 2.133, g_{yy} = 2.053, g_{zz} = 2.395, A_{xx} = 5.0, A_{yy} = 3.4, A_{zz} = 11.2$								

Table 1 Principal g and hyperfine coupling tensor (A) with direction cosines and powder spectrum values of the  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(dmen)] and [Zn(sac)<sub>2</sub>(paen)]

considered. The unpaired electron occupies mainly the  $d_{xy}(B_2)$  and  $d_{xz}$ ,  $d_{yz}(E)$  orbitals of Cu<sup>2+</sup> ion, as will be expected from pseudotetrahedral ( $D_{2d}$ ) structures.

# 3.2. $Cu^{2+}$ in $[Zn(sac)_2(paen)]$

Angular variations of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(paen)] indicate the existence of two  $Cu^{2+}$  sites as seen in the plot of angular variations of line positions in three mutually perpendicular planes of orthorhombic crystal, Fig. 6. The principal *g* and hyperfine elements are given in Table 1. The parameters are seen to be rhombic rather than being axially symmetric.  ${}^{65}Cu^{2+}$  and  ${}^{63}Cu^{2+}$ lines are not resolvable because of broad line widths.

Fig. 7 shows the powder and simulated spectrum of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(paen)]. These components of *g* and hyperfine coupling tensors are measured and given in Table 1 together with single crystal values. It is obvious that  $Cu^{2+}$  ion substitutes with

 $Zn^{2+}$  ion in the host lattice in an octahedral environment with rhombic distortion, Fig. 1.

The spin-orbit and crystal field interactions are intrinsic in g and hyperfine tensor elements. The ground state wave function of d<sup>9</sup> ions, given below, can be written as the mixture of  $d_{x^2-y^2}$  and  $d_{3z^2-y^2}$  orbitals of the central metal ion in octahedral environment,

$$\psi = k \left[ \alpha \left| \mathbf{d}_{x^2 - y^2} \right\rangle + \beta \left| \mathbf{d}_{3z^2 - r^2} \right\rangle \right]$$
(5)

where *k* is the covalency parameter which indicates the probability of finding the unpaired electron in d orbital of Cu<sup>2+</sup> ion.  $\alpha$  and  $\beta$  are the mixing coefficients of  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  orbitals having the normalization conditions:

$$\alpha^2 + \beta^2 = 1 \tag{6}$$



Fig. 6. Variation of the  $g^2$  values of all lines in three planes of Cu<sup>2+</sup> doped [Zn(sac)<sub>2</sub>(paen)] single crystal.

EPR parameters related with the structural parameters for rhombic environment are given as [16,17]

$$A_{x} = P \left[ -\kappa + \frac{k[2(\alpha^{2} + \beta^{2}) - 4\sqrt{3}\alpha\beta]}{7} + (g_{x} - g_{e}) - \frac{1}{14} \left( \frac{3\alpha + \sqrt{3}\beta}{\alpha - \sqrt{3}\beta} \right) (g_{y} - g_{e}) + \frac{\sqrt{3}\beta}{14\alpha} (g_{z} - g_{e}) \right]$$

$$A_{y} = P \left[ -\kappa + \frac{k[2(\alpha^{2} + \beta^{2}) + 4\sqrt{3}\alpha\beta]}{7} + (g_{y} - g_{e}) - \frac{1}{14} \left( \frac{3\alpha - \sqrt{3}\beta}{\alpha + \sqrt{3}\beta} \right) (g_{x} - g_{e}) - \frac{\sqrt{3}\beta}{14\alpha} (g_{z} - g_{e}) \right]$$

$$A_{z} = P \left[ -\kappa + \frac{4k(\alpha^{2} + \beta^{2})}{7} + (g_{z} - g_{e}) - \frac{1}{14} \left( \frac{3\alpha - \sqrt{3}\beta}{\alpha + \sqrt{3}\beta} \right) (g_{x} - g_{e}) + \frac{1}{14} \left( \frac{3\alpha + \sqrt{3}\beta}{\alpha - \sqrt{3}\beta} \right) (g_{y} - g_{e}) \right]$$

$$g_{x} = g_{e} + \frac{2k^{2}\lambda(\alpha + \sqrt{3}\beta)^{2}}{\Delta_{yz}}, \qquad g_{y} = g_{e} + \frac{2k^{2}\lambda(\alpha - \sqrt{3}\beta)^{2}}{\Delta_{xz}}, \qquad g_{z} = g_{e} + \frac{8k^{2}\alpha^{2}\lambda}{\Delta_{xy}}$$

$$(7)$$

*k*,  $\alpha$  and  $\beta$  are described above.  $\kappa$  is the polarization constant, *P* is dipolar hyperfine parameter for metal ion defined as  $P = kP_0$ , where free ion value  $P_0$  for <sup>65</sup>Cu<sup>2+</sup> is 388 × 10<sup>-4</sup> cm<sup>-1</sup> and for <sup>63</sup>Cu<sup>2+</sup> is 416 × 10<sup>-4</sup> cm<sup>-1</sup> [17];  $g_e = 2.0023$  the free electron *g* value;  $\Delta_{xy}$ ,  $\Delta_{xz}$  and  $\Delta_{yz}$  are the energy splittings of  $|d_{xy}\rangle$ ,  $|d_{xz}\rangle$  and  $|d_{yz}\rangle$  states with respect to ground state, and can be obtained using optical absorption spectroscopy. And, since the optical absorption spectrum is irresolvable, the energy values are calculated using Eq. (7). The values change between 11,500 and 16,000 cm<sup>-1</sup> which are in the range of the values with similar structures [17].

The wave functions of sites I and II are constructed using the calculated values as follows:

$$\Psi_{\rm I} = \sqrt{0.72} \left[ 0.994 \left| {\rm d}_{x^2 - y^2} \right\rangle + 0.105 \left| {\rm d}_{3z^2 - r^2} \right\rangle \right] \tag{8a}$$

$$\Psi_{\rm II} = \sqrt{0.83} [0.982 \left| d_{x^2 - y^2} \right\rangle + 0.188 \left| d_{3z^2 - r^2} \right\rangle \tag{8b}$$



Fig. 7. Powder spectrum (a) and simulated spectrum and (b) of  $Cu^{2+}$  doped [Zn(sac)<sub>2</sub>(paen)].

The coefficients of the both sites are seen to be slightly different indicating a small difference in the environments of both sites. The covalency parameter *k* approximately has the value of 0.72 and 0.83 for sites I and II, respectively, meaning that the unpaired electrons spend 72 and 83% of time on d orbitals of  $Cu^{2+}$  ions of both sites. The rest of the times, 28 and 13% for two sites, respectively, are spent on ligand orbitals. Similarly, the unpaired electron on d orbitals of  $Cu^{2+}$  ion for both sites spend approximately 98 and 96% of time on  $d_{x^2-y^2}$  orbitals and the rest of approximately 1 and 3% on  $d_{3z^2-r^2}$  orbitals for both sites.

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