EPR Studies of Cu^{2+} in dl-Aspartic Acid Single Crystals

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EPR studies of Cu^{2+} doped dl-Aspartic Acid [$NH_2CH(CH_2COOH)COO$] powder and single crystal have been carried out at 113 and 300 K. The principal hyperfine and g values, covalancy parameter, mixing coefficients and Fermi-contact term of the complex were obtained, and the ground-state wavefuntion of the Cu^{2+} ion in the lattice has been constructed.

Key words: Electron Paramagnetic Resonance; dl-Aspartic Acid; Amino Acid.

Introduction

Metal ion complexes, especially Cu^{2+} complexes in amino acids have revealed interesting facts [1 - 9]. The structural and electronic properties of most of the Cu^{2+} complexes in amino acids are similar, but their magnetic properties differ. X-ray diffraction studies give no information about dynamic and quantum mechanical properties, but these properties can be obtained by other techniques, among which EPR is the most suitable one.

In the present study we report EPR spectral results on Cu^{2+} in dl-Aspartic Acid single crystal and powder at room temperature and 113 K, and construct the ground-state wavefunction of the Cu^{2+} ion to explain the structural deformation.

Experimental

dl-Aspartic Acid was obtained commercially from Merck. The single crystals were grown from saturated aqueous solutions of the compound. Very small amounts of $CuSO_4$ were added to the solution as impurity, and well developed single crystals were obtained after one week. dl-Aspartic Acid is monoclinic with unit cell dimensions a = 9.15 Å, b =7.5 Å, c = 15.8 Å and β = 96°. There are 8 molecules in a unit cell [10].

The EPR spectra were recorded by a Varian Century Series X band spectrometer equipped with a Varian variable temperature control unit. The single crystal chosen for investigation was glued on a lucite pillar, which is connected to a goniometer graded in 1°. The crystal was rotated in three perpendicular planes, a^*b, ca^* and bc, respectively, with 10° intervals.

Results and Discussion

The EPR spectra of the Cu^{2+} doped dl-Aspartic Acid taken at all orientations at room temperature show two sets of four lines, which are attributed to two magnetically distinct Cu^{2+} complexes. Since the linewidth is relatively broad, the ^{63}Cu and ^{65}Cu lines are not clearly resolvable in most of the orientations, Figure 1. In all orientations, the spectra fit exactly to the properties of monoclinic symmetry [11]. Moreover, in the a^*c plane, when the magnetic field makes 45° with the c axis, superhyperfine splittings were observed, Figure 2. These splittings are actually the superposition of two *quintets* arising from magnetically equivalent nitrogen atoms in the ligands. This is the maximal nitrogen superhyperfine splitting observed and resolved. The value is about 1.2 mT. The same structure was observed in some of the Cu^{2+} complexes of amino acids and can be accepted as a characteristic feature. In 2-Methyl Alanine, α-Glycine and L-Alanine, the superhyperfine values for N atoms are between 1 and 1.4 mT [1]. They are thus consistent with our result.

The magnetic field variation of the Cu^{2+} lines with rotation in three perpendicular planes is shown in Figure 3. Neglecting the nuclear Zeeman and quadruple

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Table 1. Principal **g** and hyperfine values (**A**) and their direction cosines with respect to the a^*, b, and c axes for Cu^{2+} in dl-Aspartic Acid single crystal and spin-Hamiltonian parameters of the powder spectrum ($\Delta\mathbf{g} = \pm 0.005$, $\Delta\mathbf{A} = \pm 0.05$ mT).

Site	g	— Direction cosines — a^*	b	c	Hyperfine (**A**) mT	— Direction cosines — a^*	b	c
I	$g_{xx} = 2.075$	–0.610	0.370	–0.699	$A_{xx} = 3.86$	0.649	–0.95	0.754
	$g_{yy} = 2.034$	0.750	0.009	0.660	$A_{yy} = 8.55$	–0.751	0.042	0.655
	$g_{zz} = 2.291$	0.251	0.928	0.272	$A_{zz} = 9.96$	0.117	0.992	0.024
II	$g_{xx} = 2.099$	0.680	0.192	0.705	$A_{xx} = 3.93$	0.634	0.061	0.770
	$g_{yy} = 2.032$	–0.723	0.031	0.689	$A_{yy} = 8.47$	0.717	0.323	0.616
	$g_{zz} = 2.257$	0.141	0.979	0.165	$A_{zz} = 9.57$	0.287	–0.944	–0.160

Spin-Hamiltonian parameters of the powder EPR spectrum

$g_{xx} = 2.106$ $g_{yy} = 2.038$ $g_{zz} = 2.291$ $A_{xx} = 4.0$ mT $A_{yy} = 8.5$ mT $A_{zz} = 10.0$ mT

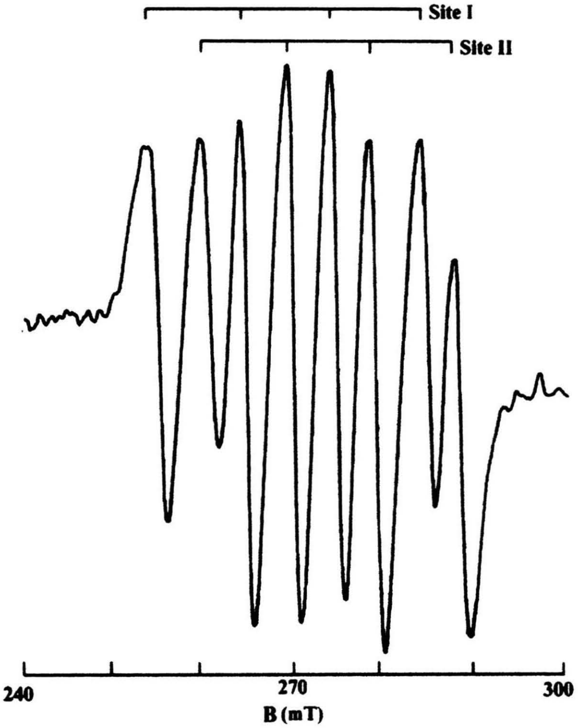

Fig. 1. EPR spectra of Cu^{2+} doped in dl-Aspartic Acid, taken in the a^*b plane making 80° with magnetic field at room temperature.

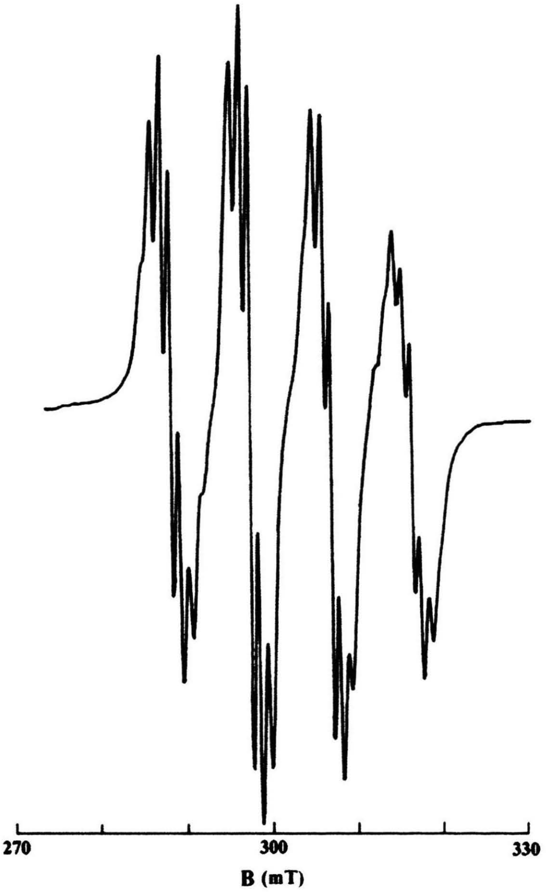

Fig. 2. Superhyperfine splittings in the EPR spectrum of Cu^{2+} doped dl-Aspartic Acid single crystal, when the magnetic field makes 45° with the c axis in the a^*c plane.

interactions, the variation fits to the Hamiltonian for rhombic symmetry,

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

The variation of lines shows no axial symmetry, so, we calculated the principal **g** and hyperfine values following Harriman's approach for second order shifts

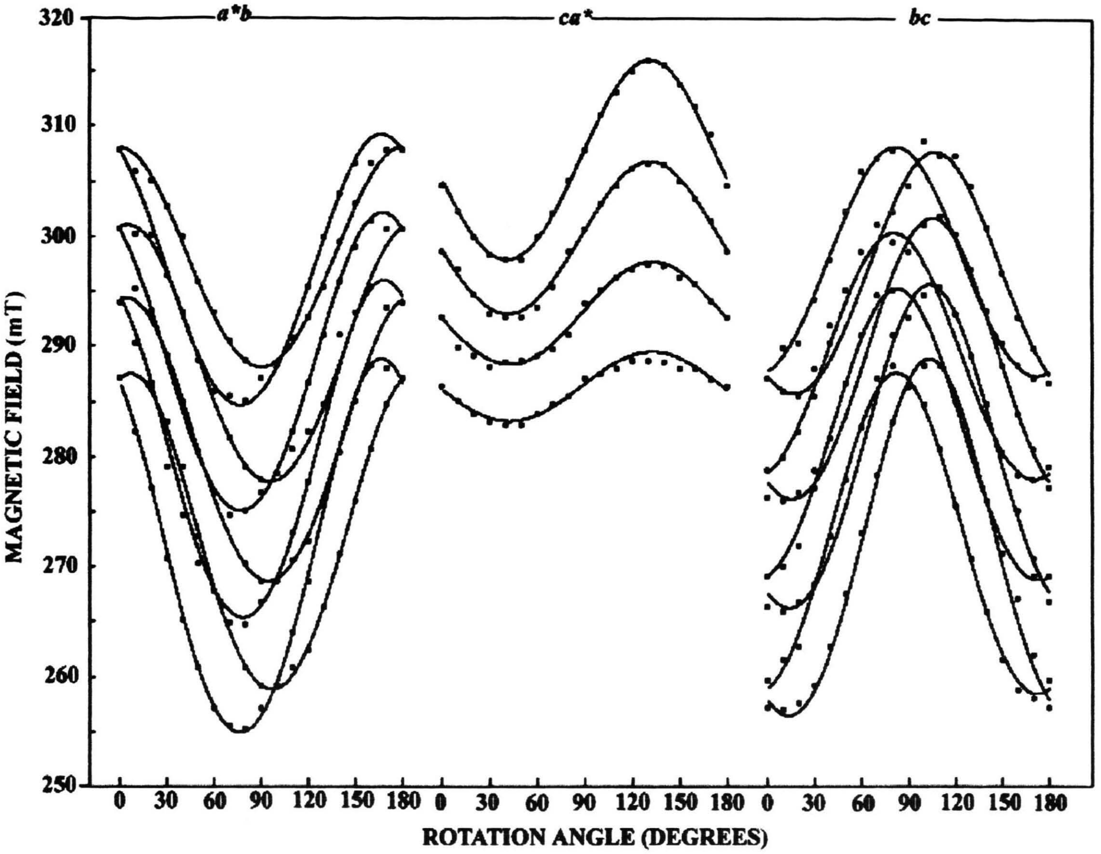

Fig. 3. The magnetic field variation with respect to rotation of the crystal in three perpendicular planes.

[12] instead of Bleaney's second order formulation for axially symmetric systems [13]. The calculated principal values and direction cosines are given in Table 1.

Figure 4 shows the powder EPR spectrum of Cu^{2+} doped dl-Aspartic acid crystal. It can be clearly seen from the powder spectrum that the complex symmetry in the crystal is not axial. The powder EPR spectrum was partially resolved into three components (g_{xx}, g_{yy}, g_{zz}). The calculated values of g_{xx}, g_{yy}, g_{zz} and the hyperfine values of A_{xx}, A_{yy} and A_{zz} are given in Table 1. These parameters are in good agreement with those obtained from the single crystal EPR data.

In contrast to such Cu-amino acid complexes as L-Alanine [1], α-Glycine [1], and L-Isoleucine monohydrate [2], the Cu^{2+} - dl-Aspartic Acid complex shows no significant change from room temperature down to 113 K. So, all measurements are made at room temperature.

It is well known that Cu^{2+} forms an octahedral complex with two of the ligands being amino groups and the other four ligands being oxygens of carboxyl groups and water molecules surrounding the Cu^{2+} ion [1, 2, 6 - 9]. The shape of the complex is given in Figure 5.

The uniaxial behavior of the hyperfine and g value variations shows that the octahedron is highly distorted, as indicated by the spin Hamiltonian parameters. It is known that, when $R = (g_x - g_y)/(g_z - g_x)$ is less than unity, the unpaired electron is dominantly in the $d_{x^2-y^2}$ state, and for R grater than unity it is in the $d_{3z^2-r^2}$ state. The observed R values for two sites, $R_{\mathrm{I}} = 0.194$ and $R_{\mathrm{II}} = 0.424$, are less than unity, and therefore the ground state of the electron is dominantly $d_{x^2-y^2}$ [16, 17]. In fact, when the site symmetry is rhombic or lower, the ground state will be neither $d_{3z^2-r^2}$ nor $d_{x^2-y^2}$ but an admixture of both [16, 17]. The distortion can be pointed out more clearly by the ground state wave function of the central Cu^{2+} ion.

Table 2. Ground-state bond parameters for Cu^{2+} ion in dl-Aspartic acid.

	α'^2	α	β	κ	δg_{cal}	δg_{exp}
Site I	0.868	0.994	0.111	0.137	0.052	0.041
Site II	0.814	0.992	0.125	0.136	0.036	0.057
Powder	0.869	0.993	0.117	0.150	0.054	0.074

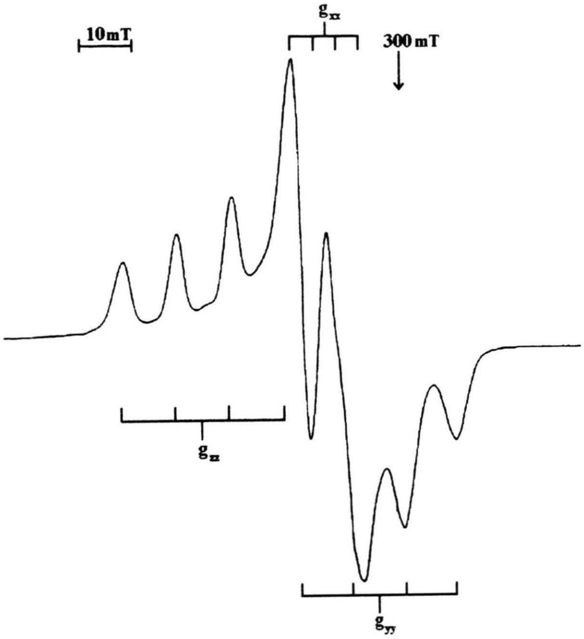

Fig. 4. Powder EPR spectrum of Cu^{2+} doped dl-Aspartic Acid recorded at room temperature.

It was Bleaney *et al.* [13] who first attempted to formulate the ground state wave function of Cu^{2+} for rhombic symmetry. In this expression, however, there were many unknown parameters, and there was no information about the covalency parameter. Later, Sroubek *et al.* [14, 15] suggested a wavefunction that contains the covalency parameter (α') and mixing coefficients α and β for the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals, respectively. Recently Bhaskar and Narayana [16] developed the most general expressions for the ground state wave function in which the covalency parameter and mixing coefficients are distinguished. The wave function is given as

$$\Psi = (\alpha'^2)^{1/2}\left[\alpha|x^2-y^2\rangle + \beta|3z^2-r^2\rangle\right].$$

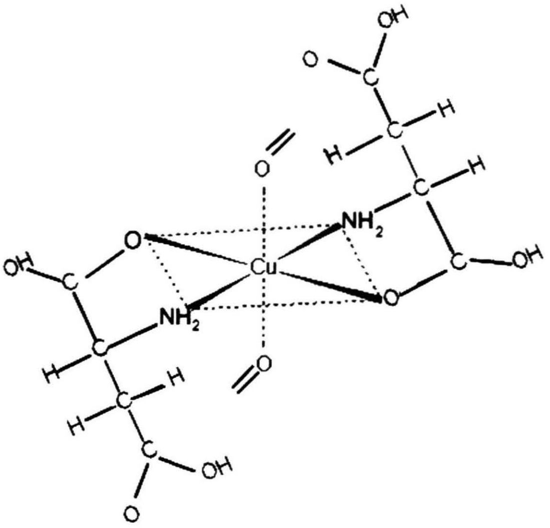

Fig. 5. Schematic illustration of the Cu^{2+} doped dl-Aspartic Acid complex.

Using the expressions given by Bhaskar and Narayana [16], α', α, β, κ and δg were calculated for both sites and for the powder spectrum. The results are given in Table 2. Using these results, the ground state wavefunction can be constructed as

$$\Psi_{\text{I}} = (0.868)^{1/2}\left[0.994|x^2-y^2\rangle + 0.111|3z^2-r^2\rangle\right],$$

$$\Psi_{\text{II}} = (0.814)^{1/2}\left[0.992|x^2-y^2\rangle + 0.125|3z^2-r^2\rangle\right],$$

$$\Psi_{\text{powder}} = (0.869)^{1/2} \cdot \left[0.993|x^2-y^2\rangle + 0.117|3z^2-r^2\rangle\right].$$

The covalency parameter $\alpha'^2 = 0.868$ obviously explains that the unpaired electron spends 13.2% of its time on ligand orbitals, whereas the rest is spent on the Cu d orbital for the site I. For site II the unpaired electron spends 18.6% of its time on ligand orbitals and 81.4% on the Cu d orbitals. The powder sample shows similar properties with site I. Since the coefficient of $d_{x^2-y^2}$ is significantly grater than that of $d_{3z^2-r^2}$, ($\alpha \approx 1$, $\beta \approx 0$) [16], one can conclude that the rhombic distortion results dominantly from $d_{3z^2-r^2}$ orbital of the Cu^{2+} ion.

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