

EPR Study of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ Complex

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Abstract. The single crystal of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ (Him: $\text{C}_3\text{H}_4\text{N}_2$, imidazole) complex has been investigated at ambient temperature in three mutually perpendicular planes by EPR technique. The magnetic environments of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex have been identified by EPR technique. The study reveals the existence of two magnetically inequivalent Cu^{2+} sites. The principal values of g tensors were obtained. The EPR parameters show that the paramagnetic centers have rhombic symmetry.

Keywords. EPR, imidazole, Cu^{2+} , spin-spin interaction.

1. Introduction

The imidazole and imidazole derivatives ligands play an important role in the coordination chemistry [1]. Methyl imidazole and its derivative is extremely important biologically becomes one tooth ligand coordinated to the metal atom through the nitrogen atom. They are used in the in pharmacy, industry, electrochemical hybridization indicators and electroactive markers of DNA in many types of intensive imidazole derivatives [2-11]. Overall it is a very large work area of the imidazole complex. These are electronic structure solutions, analysis of spectroscopic and magnetic properties are most important. In this study, the EPR investigation of single crystal $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex has been performed g parameters have been calculated.

2. Experimental

EtOH solution of Him (0.6 g, 8.8 mmol) and EtOH solution of CuBr_2 (0.5 g, 2.2 mmol) was stirred at room temperature. After about six weeks, dark blue crystals of the $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex suitable for EPR analyses were collected. $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex has monoclinic space group $C2/c$ and the unit cell parameters are $a=14.739(4) \text{ \AA}$, $b=9.029(1) \text{ \AA}$, $c=14.269(4) \text{ \AA}$, $\beta=115.95(1)^\circ$ and $Z=4$ [12].

EPR spectra were recorded on a Varian E-109C EPR spectrometer.

3. Results and discussion

$[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ single crystal of suitable size are selected to record spectrum for every 30° angle between 0° and 180° by rotating the crystal in a^*c , ba^* and cb planes at room temperature. The EPR spectra of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex in Figure 1a when the magnetic field is in a^*b plane 0° from a^*



axis, in Figure 1b when the magnetic field is in cb plane 30° from b axis. The angular variation of g^2 a^*c , ba^* and cb planes are shown in Figure 2.

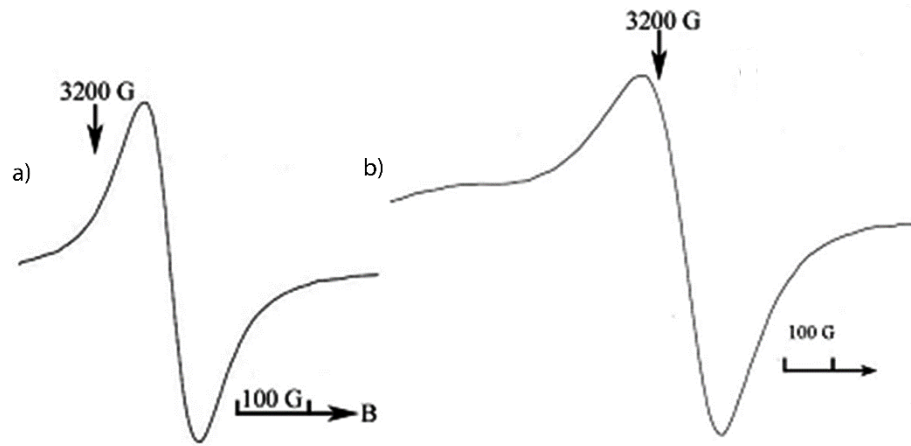


Figure 1. a) EPR spectra of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ single crystal when the magnetic field in the a^*c plane 0° away from the a^* -axis. b) EPR spectra of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ single crystal when the magnetic field in the cb plane 30° away from the b -axis.

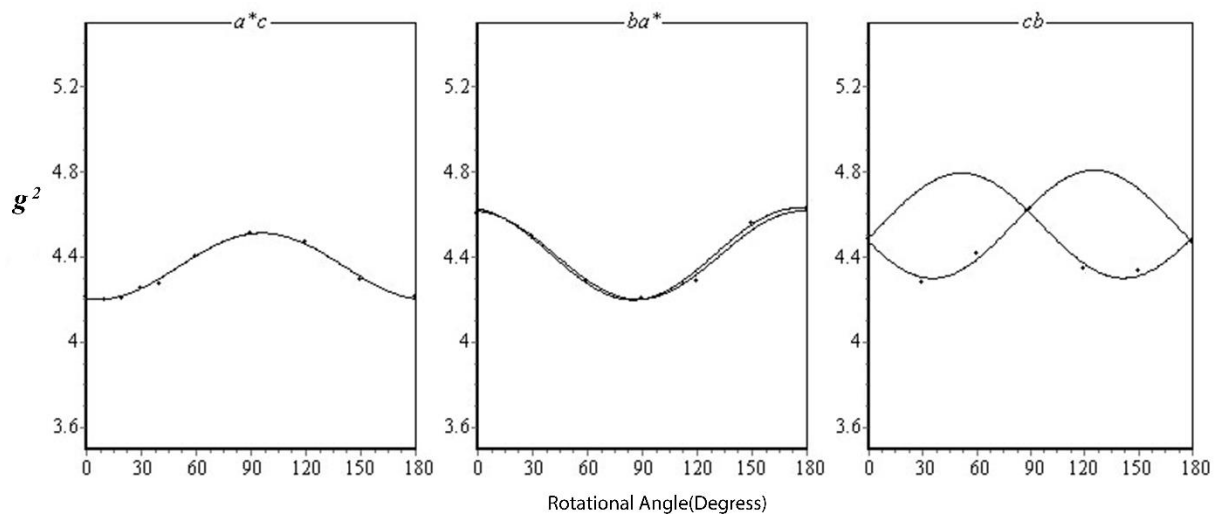


Figure 2. Angular variations of the EPR spectra of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ single crystal.

Since $S=1/2$ and $I=3/2$ for Cu^{2+} ion, the spectrum consist of four lines. But, the EPR spectra of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex has one line in all orientation. It is considered that this is due to the spin-spin interaction and spin-lattice coupling. The angular variations of g^2 in three mutually perpendicular planes are shown in Figure 2. The angular variation of g^2 values for a specific line fits to the following the expression which is valid for each plane:

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

In this equation, $i, j, k = x, y, z$ represent laboratory coordinates. θ is the rotation angle. g_{ii}^2 , g_{jj}^2 and g_{ij}^2 correspond to tensor elements of g which can be found by a fitting procedure [13].

The principal values of g tensor for $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex was evaluated by considering the following spin Hamiltonian,

$$\mathcal{H} = \beta(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z \quad (2)$$

The Hamiltonian includes electron Zeeman and hyperfine interactions. To find g value, we have used an iterative numerical technique [14]. g tensors are constructed and diagonalized to find their principal values and the results are found to indicate rhombic symmetry. The calculated g parameters are given in Table 1. From this table, we deduce that the $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ complex has an octahedral environment with a rhombic distortion. This behaviour of the spectra corresponds to a paramagnetic sample with monoclinic crystal symmetry.

Table 1. Principal g values and their direction cosines of $[\text{Cu}(\text{Him})_4] \cdot 2\text{Br}$ single crystal ($\Delta g = \pm 0.0005$).

Site	g	Direction cosines		
		a	b	c
I	$g_x=2.050$	0.997	0.054	0.061
	$g_y=2.077$	-0.005	0.784	-0.621
	$g_z=2.193$	-0.082	0.619	0.781
II	$g_x=2.048$	0.957	0.237	0.169
	$g_y=2.079$	-0.291	0.762	0.578
	$g_z=2.193$	0.008	-0.602	0.798

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