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Electron Paramagnetic Resonance Studies on cis-catena-sulphato-aqueotris (imidazole) copper (II) Exchange interactions mediated thro'sulphato bridges

K. Vijayaraj[1], A. Jawahar[1*], R. Anantharam[2], M. Kumara Dhas[3]
[1]*Department of Chemistry, NMSSVN College, Nagamalai, Madurai-625 019, Tamilnadu, India*
[2]*Department of Chemistry, ANJA College, Sivakasi, Tamilnadu, India*
[3]*Department of Physics, NMSSVN College, Nagamalai, Madurai-625 019, Tamilnadu, India*

Abstract: *Single crystal EPR and powder EPR of sulphto bridged Cu(II) complex were studied at X-band frequency. EPR of powder samples exhibit a single exchange narrowed resonance at 300 K and an orthorhombic spectrum at 77 K. Single crystal spectra show a single exchange - collapsed resonance line for all the orientations indicating the complex to be in the strong exchange regime. The magnitude of intrachain exchange coupling constant, J=0.1154(4) cm^{-1}, calculated from the angular variation of the line width clearly reveals strong coupling between the magnetic Cu(II) centers. The ratio of interchain/intrachain = 3.5 x 10^{-2} and lineshape analysis is indicative of quasi two dimensional behaviour of the system. The interchain super exchange pathway is provided by H-bonding.*

Keywords: *X-band EPR; Exchange interactions, Quasi-2D system, Cu(II) imidazole complex*

I. Introduction

Iimidazole ligated Cu(II) complexes have received much attention because of the possibility that they may mimic the active sites in copper proteins and enzymes [1-7]. These complexes also act as attractive model systems for understanding the electronic and magnetic properties, and also the exchange interactions between metal ions in metalloproteins [8-11]. Magnetic susceptibility and EPR spectroscopic techniques are particularly suitable for studying exchange phenomena [12-16]. The former is well suited for studying weak exchange coupling of order $J > 5$ cm^{-1} [12, 17, 18]. On the other hand, EPR allows one to evaluate weak exchange from data taken at high temperature. For example, weak magnetic interactions in transition metal complexes bridged by intervening ligands such as carboxylate [11, 14, 19], triazole [20, 21], azide [7, 19], pyrazole [20-24] etc have been studied by EPR. Tetraoxo anions such as phosphate, arsenate, vanadate, sulphate and molybdate are known to bridge mental centers [25]. However, studies on magnetic interactions mediated through tetraoxo anions are limited. Here, we report the EPR of a sulphato bridged Cu(II) complex, cis-catena-µ-sulphato-aquotris(imidazole)copper(II), $Cu(H_2O)(C_3H_4N_2)_3SO_4$ (hereafter referred to as SAICU). Lineshape analysis, angular variations of g-value and line width of the single exchange collapsed EPR line are used to obtain information about the dimensionality of the exchange coupled network as well as the local magnetic interactions. Also, the ability of sulphato and hydrogen bond bridges to provide intrachain and interchain super exchange interaction between Cu (II) ions is analyzed. The molecular g-factors are calculated from the crystal g-tensors and compared with those of obtaining from Cu (II) doped diamagnetic lattice.

II. Materials and Methods

2.1 EPR Measurements

Single crystals of SAICU were prepared according to the literature method [26]. EPR spectra were recorded at 300K on a Varian E-112 spectrometer operating at X-band frequency. Single crystal EPR measurements were performed by rotating the crystal around three mutually perpendicular axes, viz., the crystal a, b and c* axes, where c* is perpendicular to a and b, to derive the principal values of the magnetic tensors. Angular variations were recorded at every 10º interval. Diphenylpicrylhydrazyl (DPPH, g = 2.0036) was used as an internal field marker. The field calibration of the instrument was periodically checked using a standard sample of Mn(II) in MgO. The error in the peak-to-peak line width (ΔB_{pp}) is ±1. The paramagnetic susceptibility of SAICU was determined by the Guoy method at 300K in an applied field of 800 mT. Mercury (II) tetrathiocyanatocobaltat(II) was used as the calibrant.

III. Results and Discussion

3.1 Crystal structure and superexchange pathway

The crystals of SAICU [26] are reported to be monoclinic of space group $P2_1/n$ with the unit cell parameters a = 14.239(1), b = 8.707(1) and c = 11.717(1) Å, $\beta = 90.244(3)^{\circ}$, Z = 4. The Cu(II) ion is at the centre of a distorted octahedron (Fig. 1), formed by three nitrogen atoms from three imidazole molecules, one oxygen from a water and two oxygen atoms from two sulphate groups. The packing diagram of the molecules viewed along a axis is shown in Fig. 2. The structure consists of 1D infinite polymeric chains of $Cu(H_2O)(C_3H_4N_2)_3$ units bridged by sulphato ligand. These chains run in the b-direction along the twofold screw axis. The adjacent Cu(II) chains are held together by the following hydrogen bonds, N(6)-H(12)…O(1) = 2.762(4) Å and O(5)-H(13)…O(4) = 2.183(4)Å. The interchain Cu-Cu separation is 8.547 Å while the intrachain Cu-Cu distance is 6.047 Å.

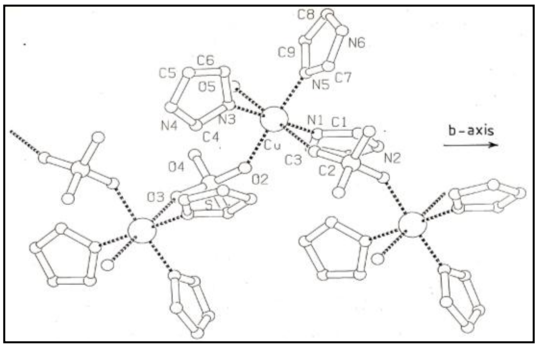

Fig. 1 *A Pluto diagram of SAICU generated using the data in Ref.26 showing the coordination around Cu(II) as well as the sulphato between Cu(II) moieties.*

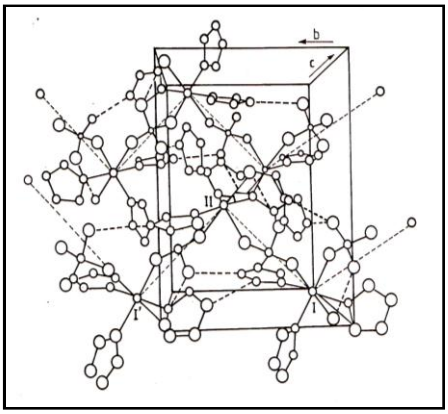

Fig. 2 *Extended packing diagram of the Cu(II) complex down a- axis showing 1D infinite Polymeric chains of $Cu(H_2O)(C_3H_4N_2)_3$ units bridged by sulphato ligand. Hydrogen bonding interactions between the adjacent chains are shown as dotted line. Carbon, Hydrogen and uncoordinated nitrogen atom are excluded for clarity.*

3.2 EPR Spectroscopy

3.2.1 Powder EPR

All EPR spectra of polycrystalline samples of the Cu(II) complex, SAICU recorded at 300 K (shown in Fig. 3a) is typical of a magnetically concentrated system. A single broad line is obtained and the g-anisotropy is not resolved, indicating a strong exchange interaction between neighbouring Cu(II) centers. However, at 77 K, an orthorhombic spectrum (Fig. 3b) with three well resolved g-features, $g_1^{ex} = 2.2678$, $g_2^{ex} = 2.1236$, $g_3^{ex} = 2.0770$, indicating the low symmetry of the complex, is observed. No half-field transition ($\Delta m_s = 2$) was detected at g = 4, revealing the absence of dipole-dipole interaction between two consecutive crystallographically independent Cu(II) centers. The magnetic moment value of 1.55 μ_B for SAICU, measured at 300 K, is typical of a polymeric complex with antiferromagnetic interaction.

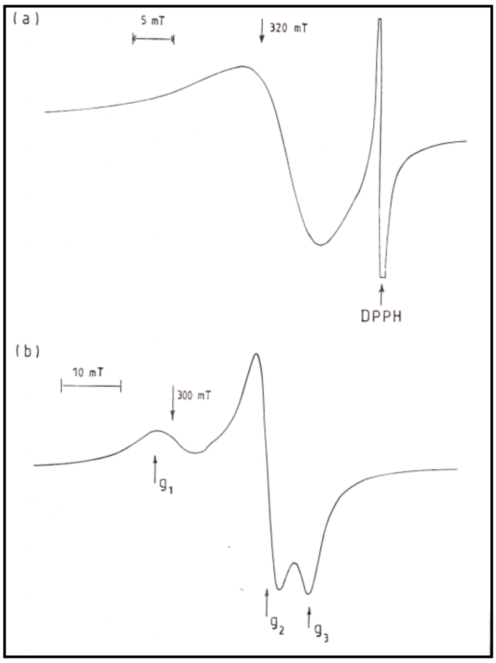

Fig. 3 *X – band power EPR spectra of SAICU at a) 300 K and b) 77K*

3.2.2 Single Crystal EPR

The single crystal EPR spectra of SAICU at X-band showed a single resonance line for any orientation of the applied field. Except for rotation about b- axis, two EPR signals are expected due to the presence of two magnetically distinct sites in the unit cell (Fig. 2). The exchange interaction is strong enough to produce a complete merging of the hyperfine splitting lines and also average the signals from the two magnetically inequivalent sites. Hence, it follows

$$\text{A (hyperfine), D(dipolar)} < \Delta g\beta B_0 < J' \text{ (X-band)} \qquad (1)$$

The single crystal EPR spectra may be fitted to the spin Hamiltonian as follows [17]

$$H = \mu_B S.g.B \qquad (2)$$

Where S is the effective spin (S = ½), B is the external applied magnetic field, g is the tensor describing the angular variation of the g factor, and μ_B is the Bohr magneton. The angle-dependent g-value based on equation (2) is given by

$$g^2(\theta) = (g_1^2 \cos^2 \theta_1 + g_2^2 \cos^2 \theta_2 + g_3^2 \cos^2 \theta_3)^{0.5} \qquad (3)$$

The principal crystal g-tensors and their direction cosines in the orthogonal framework (a, b and c*) were evaluated using Schonland method [27] and are listed in Table 1. The observed and calculated (using the observed direction cosines in Table 1), angular variations of g in all the three planes are shown in Fig. 4. There is a good agreement between the calculated and experimental values. The crystal g-values, thus obtained, $g_1^{ex} = 2.2678$, $g_2^{ex} = 2.1236$, $g_3^{ex} = 2.0770$ are exchange influenced. So, an attempt was made here to calculate the molecular g-tensor from the experimental crystal g-tensor. From the exchange-influenced g-values, the canting angle 2α can be calculated [28] by using the equation (4).

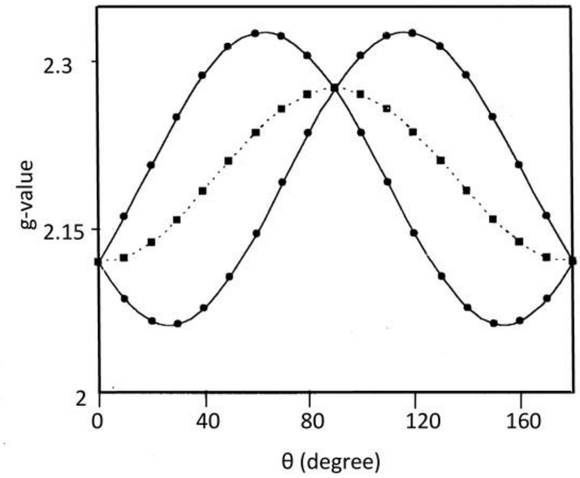

Fig. 4: *Angular variation of g-factors for the magnetic field applied in the three crystalline planes of signal crystal of SAICU (■-ab plane, ■-bc*plane, Δ -ac* plane). The solid lines were obtained with the parameters in Table 1.*

$$\mathrm{Cos}\ 2\alpha = (g_1^{ex} - g_2^{ex}) / (g_1^{ex} + g_2^{ex} - 2g_3^{ex}) \qquad (4)$$

The calculated canting angle, 51.6° is in agreement with X-ray data (Table 2). Molecular g-values, g_1, g_2 and g_3 were estimated by using the following relations

$$g_1^{ex} = g_1(\cos^2\alpha) + g_2(\sin^2\alpha)$$
$$g_2^{ex} = g_2(\cos^2\alpha) + g_1(\sin^2\alpha)$$
$$g_3^{ex} = g_3 \qquad (5)$$

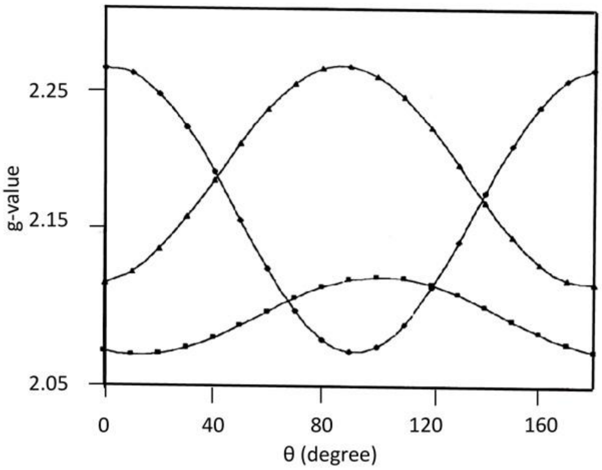

Fig. 5 : *Calculated (—) and experimental (•••) of angular variation of the g-Factors for rotation in ab plan for Cu(II) doped Cd(II) analog. The average g-values obtained (---) match well with the experimental (■■■) g-factors for SAICU revealing the exchange averaging of two magnetic sites.*

The molecular g-values derived using the experimentally obtained exchange-averaged g-values, are g_1= 2.3242, g_2 = 2.077 and g_3 = 2.0450. The molecular g-values, thus derived from the experimental crystal g-tensor listed in Table 2, which is close to the actual experimental molecular g-values obtained from the diamagnetically diluted system, Cu(II)/SAICU [29]. Using the molecular g-values and their eigen vectors obtained from the dilute system, the angular variations of g for two magnetically distinct sites were simulated. The average g-values for the two magnetic sites for a typical ab plane as shown in Fig. 5 agree well with the experimental "exchange-averaged" g-values. Thus, the observation of single resonance line can be rationalized based on the exchange averaging of the two magnetic sites.

Table 1 Values of the components of the crystal g tensor and their eigen vectors in the a, b and c* framework

Principal axes	Eigen values	Eigen vectors
g_1^{ex} =	2.2678	0.9921, -0.0293, 0.1220
g_2^{ex} =	2.1236	0.2290, 0.9669, -0.1122
g_3^{ex} =	2.0770	-0.2239, 0.0562, 0.9730

Table 2 The molecular g-factors and the canting angle 2α between the molecular axes of the two magnetic Cu(II) sites.

Compound	g_1^{mol}	g_2^{mol}	g_3^{mol}	2α
SAICU	2.3242	2.0770	2.0450	51.6°[a] 52.3°[b]
Cu(II)/ SAICU	2.3273	2.0880	2.0440	-

[a]from X – ray data [b] from EPR data

3.2.3 Evaluation of inter and intrachain Exchange

For magnetically concentrated systems, the line width (ΔB_{pp}) of the EPR spectra depends on two factors, viz., the dipolar interaction which broadens the resonance and the exchange interaction which narrows the resonance line [17]. The line width in three dimensional systems is narrow due to the domination of exchange effects [12, 17]. The exchange effect is less in low dimensional systems, producing line widths of intermediate nature. The dimensionality of a system can be characterized largely by the angular dependence of the line width. In general, the line width follows ($1+\cos^2\theta$) or $(3\cos^2\theta-1)^2$– $(3\cos^2\theta-1)^{4/3}$ angular dependence in three or two or one dimensional systems respectively [30]. The line width variation, in the case of SAICU, follows the $(3\cos^2\theta-1)^2$dependence. The typical angular variation of the line widths for the ac* plane, given in Fig. 6, follows $(3\cos^2\theta-1)^2$ dependence, indicating the two dimensional characteristics of the system. To gain a deeper insight into the mechanism of superexchange interaction [12], an attempt was made to analyze the line width anisotropy, by examining the contribution of various terms to the second moment. The total moment, $M_2^{(t)}$, is given by

$$M_2^{(t)}= M_2^{(0)}+ M_2^{(1)} + M_2^{(2)} + a^{(0)}+ a^{(1)} \qquad (6)$$

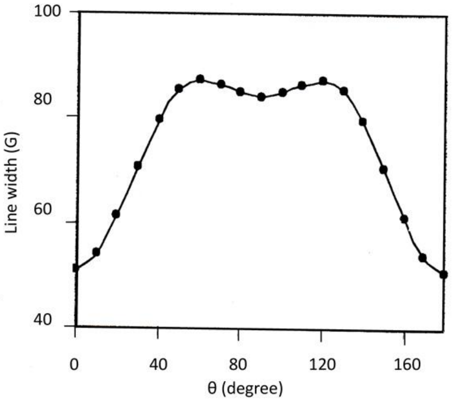

Fig. 6: *Typical angular variation of the peak-to-peak line width of SAIUC for the magnetic field applied in ac* plane. The solid line is simulated by using eq.(6).*

Here $M_2^{(0)}$, $M_2^{(1)}$and $M_2^{(2)}$ represent the dipolar second moments due to the transitions $\Delta m = 0$ (secular), $\Delta m = \pm 1$ and $\Delta m = \pm 2$ respectively. $a^{(0)}$ and $a^{(1)}$ represent the hyperfine second moments. The second moment, which is a measure of line width, has thus secular and non-secular contributions. The secular contribution of the dipolar second moment for S = ½ is given by

$$M_2^{(0)} = (9/16)g^4\beta^4 \sum_{i\neq j} (3\cos^2\theta_{ij}-1)^2 r_{ij}^{-6} \qquad (7)$$

Where $g^2 = (g_1^2+ g_2^2 + g_3^2) / 3$, r_{ij} is the distance between the interacting copper atoms and θ_{ij} is the angle between r_{ij} and the effective field $g.B_o$. The non-secular second moments $M_2^{(1)}$ and $M_2^{(2)}$ are given by

$$M_2^{(1)}=(9/16)g^4\beta^4 \sum_{i\neq j} \sin^2\theta_{ij}\cos^2\theta_{ij} r_{ij}^{-6} \qquad (8)$$

$$M_2^{(2)} = (9/16)g^4\beta^4 \sum_{i\neq j} \sin^4\theta_{ij}\, r_{ij}^{-6} \qquad (9)$$

To estimate the secular contribution of the dipolar second moment, the lattice sum $\Sigma(3\cos^2\theta_{ij}-1)^2\, r_{ij}^{-6}$ was computed, using crystal structure data, for the bc* plane. From the lattice sum thus obtained, $M_2^{(0)}$ was computed using equation (7). A similar procedure was followed to calculate $M_2^{(1)}$ and $M_2^{(2)}$. The attempt to correlate the theoretical local fields with the experimental line widths yielded no satisfactory fit, revealing that dipolar interaction is not the only factor contributing to second moment. According to Date et al [31], the second moment, involving both dipole-dipole and exchange interaction, is given by

$$M_2 = 0.75S\,(S+1)\,[A^2\{1+\cos^2(\varepsilon-\theta)\} + 4B^2\ (1+\cos^2)-AB\{1+3\cos^2(\varepsilon-\theta)\,(3\cos^2\theta-1)\}] \qquad (10)$$

Where $A = A_{zz}$, $B = g\beta/r_0^3$. Hence r_0 is the distance between the copper atom at the origin and its nearest neighbour, $(\varepsilon - \theta)$ is the angle between the magnetic field and projection of the tetragonal axis in the plane of rotation. In the present case, θ has been measured from b-axis towards a-axis in the ab-plane. The local fields calculated using equation (10) matched well with the experimental values (Fig. 7), which reveals the contribution of anisotropic exchange. For a weak two-dimensional exchange system, the peak-to-peak line width (ΔB_{pp}) is related to the exchange coupling by

$$(\sqrt{3}/2)(\Delta B_{pp}) = M_2^{(t)}/J \qquad (11)$$

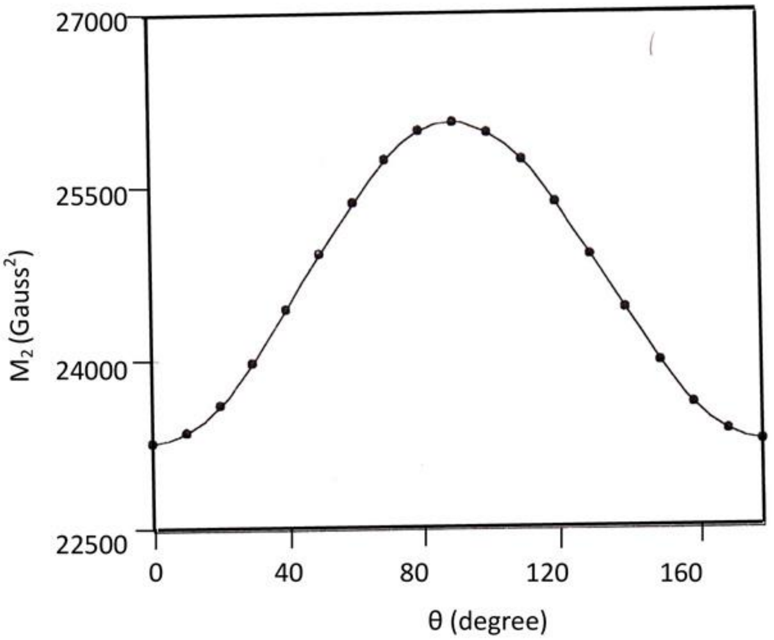

Fig. 7 *Angular variation of local fields (—) calculated by Date's method and observed line Width (•••) in bc* plane.*

Using equation (11), the interchain exchange coupling, J was computed to be 0.1154(4) cm^{-1} indicating a strong exchange between the Cu(II) ions mediated through the sulphato bridge. The interchain exchange parameter, J' may be estimated from the relation [12]

$$\tau_c = 0.16\, h\, |J|^{1/3} / |J'|^{4/3} \qquad (12)$$

Where τ_c is the spin correlation time given by $\tau_c = 3.464\, h/g\beta H_e$ and H_e is the effective intersite exchange field, which may readily be obtained from the angular variation of the line width. For $J' > (\Delta g)\, \beta\, B / 2$, the width of the line varies as the square of the splitting ΔB (in Gauss) between the sites.

$$\Delta B_{pp} = (\Delta B)^2 / H_e \qquad (13)$$

The calculated H_e = 116 G gives a value of 1.5 x 10^{-10} s for τ_c which leads to a J' value of 0.004(3) cm^{-1}. This interchain exchange may be largely attributed to superexchange interactions (vide supra) arising from intermolecular H-bonding. The ratio of J'/J =3.5 x 10^{-2} is relatively large enough to make the interactions quasi-2D in agreement with the X-ray data.

3.2.4 Lineshape analysis

For low dimensional systems, the exchange is less effective due to the restricted exchange pathways for spin diffusion [12]. This results in slow spin deviation, making the spin correlation to persist for extremely long times and hence, leads to non-Lorentzian lineshape [32,33]. Thus, the EPR lineshape of low dimensional systems is intermediate between Lorentzian and Gaussian. To examine the spin diffusion effects on EPR lineshapes, the derivative intensity, $[I'_{p(B-Bo)}/I'_{(B-Bo)}\ \Delta B_{pp}]^{1/2}$ may be plotted against $[(B-Bo)/\Delta B_{pp}]^2$. The results of lineshape analysis for SAICU are presented in Fig. 8 for two typical orientations B ‖ a ($\theta = 90^\circ$) and B ‖ b ($\theta = 0^\circ$) in the ab-plane. When the magnetic field is parallel to a-axis, the lineshape deviates considerably from Lorentzian but it is nearly Lorentzian, when the applied field is parallel to b-axis. When B makes an angle of 55° with the normal to the two-dimensional magnetic plane, the lineshape function is Lorentzian in nature. These results indicate that the long time behaviour of spin correlation functions is operative in SAICU, as expected for a quasi-two-dimensional systems.

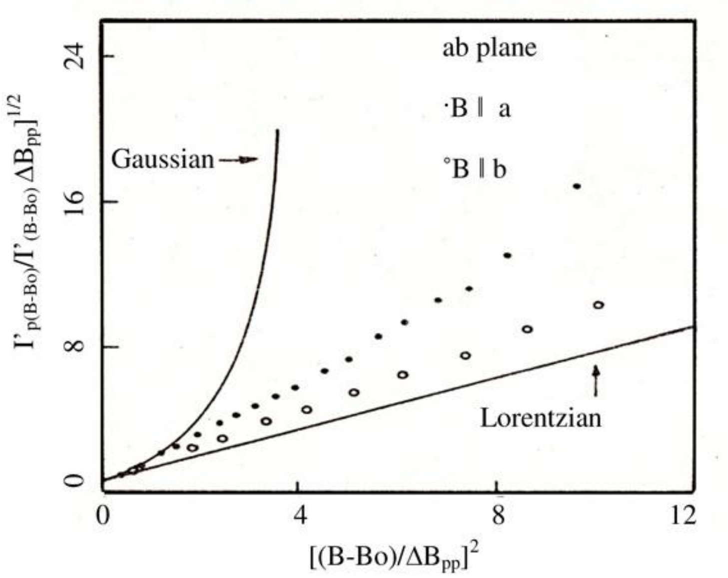

Fig. 8 *EPR lineshape analysis of X-band spectra of two typical orientations B ‖ a (θ=90°) and B ‖ b (θ =0°) in ab-plane along with the Gaussian and Lorentzian lineshapes. The solid line is a guide for the eye.*

IV. Conclusion

X-band EPR of single crystals of a sulphato bridged Cu(II) complex is reported. The observation of a single exchange-collapsed resonance line for all the orientations reveals the complex to be in the strong exchange regime. The line width anisotropy is successfully fitted based on Date's equation incorporating contribution from both dipolar and anisotropic exchange. An estimate of the magnitude of intrachain exchange coupling constant, $J = 0.1154(4)\ \text{cm}^{-1}$ is indicative of strong coupling between the magnetic Cu(II) centers mediated through sulphato bridges. The ratio $J'/J = 3.5 \times 10^{-2}\ \text{cm}^{-1}$ and lineshape analysis support quasi two-dimensional behaviour of the system. The H-bonding interactions between the chains provide superexchange pathway leading to quasi 2D behaviour.

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