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Non-secular ESR broadening in a copper–amino acid complex

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Abstract. Single crystal ESR measurements at 33.6 GHz (Q band) in the layered copper–amino acid complex bis(L-Phenylalaninato)copper(II), $Cu(L\text{-}Phe)_2$, are reported and compared with earlier results at 9.7 GHz (X band). Strong frequency-dependent effects were observed in the linewidth, which were isolated by subtracting the Q-band data from the X-band ones. The difference data were least-squares fitted to a theoretical expression including non-secular contributions of the different interactions present in this exchange-coupled system, plus a secular contribution ('residual Zeeman') due to the existence of two copper sites with different orientations. The weight of non-secular contributions allowed us to estimate an exchange frequency $\omega e/2\pi = (10 \pm 2)$ GHz in $Cu(L\text{-}Phe)_2$, which involves the interaction with the six copper neighbours. The frequency related with the exchange interaction between non-equivalent copper neighbours only, $\omega e_{AB}/2\pi = (10.7 \pm 0.6)$ GHz, was calculated from the secular residual Zeeman contribution. These values indicate that the spin dynamics in $Cu(L\text{-}Phe)_2$ is mainly determined by the exchange interaction between non-equivalent copper neighbours.

1. Introduction

Magnetic studies of single crystals of copper–amino acid complexes have been performed in the last few years [1–5], showing interesting physical properties. Amongst these, their layered structure leads to a low-dimensional magnetic behaviour, while the small value of the exchange interactions, of the order of tenths of a degree Kelvin [1–5] produces frequency-dependent effects in the ESR spectra [4, 5].

Recently, we reported ESR experiments on single crystals of $Cu(L\text{-}Met)_2$ [4] and $Cu(L\text{-}Leu)_2$ [5], performed at two microwave frequencies: $\omega_{0X}/2\pi = 9.7$ GHz (X band) and $\omega_{0Q}/2\pi = 33.6$ GHz (Q band). The angular variation in the linewidth was analysed taking into account the contributions of the perturbative interactions—magnetic dipolar, hyperfine, antisymmetric exchange, and that arising from the existence of two magnetically inequivalent copper sites in the lattice, called a 'residual Zeeman' interaction [4, 5]. The frequency dependence of the linewidth caused by the last contribution was explicitly analysed in [4], where we showed how the exchange interaction, J', between non-equivalent coppers may be calculated [4, 5].

In the present work we analyse non-secular contributions, which constitute another source of frequency dependence of the linewidth, broadening the ESR line when the microwave frequency is too low to average them out [6–8]. This non-secular broadening

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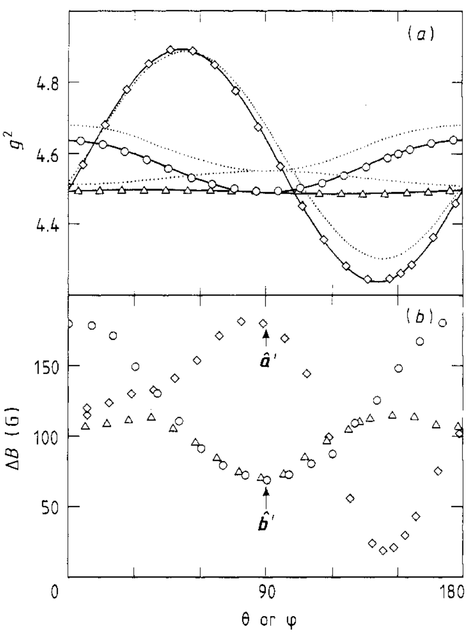

Figure 1. (*a*) Angular variation of the squared gyromagnetic factor measured at Q band (33.6 GHz) and room temperature in three orthogonal planes of Cu(L-Phe)$_2$: ○, *a'b* plane; △, *bc* plane; ◇, *a'c* plane; solid line, curves obtained using the Q-band g^2-tensor data of table 1; broken line, X band (9.7 GHz) g^2 data [3]. $\theta = 0°$ corresponds to $\hat{c}$ for the *bc* and *a'c* planes. (*b*) Angular variation of the peak-to-peak linewidth measured at Q band. The symbols are the same as in (*a*).

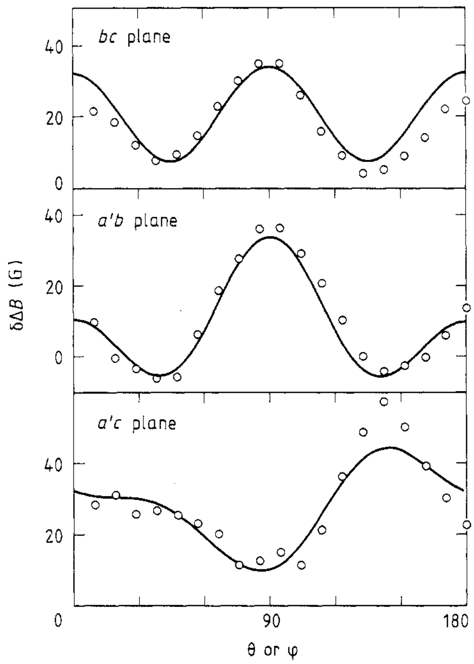

Figure 2. Angular variation of the linewidth difference $\delta\Delta B = \Delta\beta_X - \Delta\beta_Q$ between data taken for the X and for the Q band for Cu(L-Phe)$_2$. The solid curves correspond to (7) calculated with the least-squares parameters of table 2.

is highly anisotropic, and can be shown by subtracting the linewidth data at both frequencies. Our study has been performed in the complex Cu(L-Phe)$_2$, whose ESR Q-band data are reported here.

X-band data were reported in [3]. As other compounds [4–5], Cu(L-Phe)$_2$ crystallises in the monoclinic P2_1 space group, with two molecules per unit cell, related by a 180° rotation about the $\hat{b}$-axis. Cu(II) ions are arranged in layers parallel to the *bc* plane, having six Cu(II) nearest neighbours at about 5.5 Å. Two of them are in equivalent sites, and four are in rotated sites. The connections to the nearest neighbours are hydrogen and carboxylate bridges, which provide electronic paths for superexchange.

2. Experimental data

Q-band room-temperature ESR measurements were performed on single crystals of Cu(L-Phe)$_2$, grown as reported in [3]. The experimental details are the same as in [3].

A single ESR line is observed for any orientation of the magnetic field $\boldsymbol{B}$. The linewidth is strictly Lorentzian in the interval $|B - B_0| < 1.4\,\Delta B$, where B_0 is the resonance field and ΔB is the peak-to-peak linewidth. The experimental values of the squared Q-band gyromagnetic factor $g^2(\theta, \varphi)$ measured in the three perpendicular planes *a'b*, *bc* and *a'c* are displayed in figure 1(*a*). In this figure we also display X-band values, plotted as

Table 1. Values of the components obtained from the least-squares fit of a second tensor $\mathbf{g}^2$ to the experimental data of the squared gyromagnetic factor of figure 1(*a*). X-band results [3] are also included. The reference system is $xyz = a'bc$. The absolute error is 0.001 in all cases and was calculated from the dispersion of the fit.

	Q band	X band
g_{xx}^2	4.633	4.681
g_{yy}^2	4.489	4.552
g_{zz}^2	4.501	4.512
$g_{xy}^2 = g_{yz}^2$	0.001	0.000
g_{zx}	0.322	0.280

a broken line. The peak-to-peak linewidth angular variation $\Delta B(\theta, \varphi)$ is shown in figure 1(*b*). Figure 2 displays the difference in linewidths $\delta\Delta B = \Delta B_X - \Delta B_Q$. It can be seen in figure 2 that the Q-band linewidths are smaller than the X-band values for almost any orientation of B.

As in previous works [2–5, 9], the g^2 data were least-squares fitted to the function $\mathbf{g}^2(\theta, \varphi) = \hat{\boldsymbol{h}}\mathbf{gg}\hat{\boldsymbol{h}}$, where $\hat{\boldsymbol{h}} = \boldsymbol{B}/|\boldsymbol{B}|$, corresponding to the angular variation of a second order tensor $\mathbf{g}^2$. The parameters resulting from the fit are given in table 1, where X-band parameters [3] are also included to show the frequency dependence. The full curves in figure 1(*a*) were calculated using the above expression, with the Q-band parameters given in table 1.

3. Theory

To understand the frequency dependence of the non-secular effects in the ESR spectrum, we resort to the general theories of magnetic resonance in exchange-coupled systems [6, 7, 10]. The Hamiltonian of such a system in a magnetic field can be written $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'$, where $\mathcal{H}_0 = \mathcal{H}_Z + \mathcal{H}_{ex}$, where $\mathcal{H}_Z$ is the Zeeman interaction, $\mathcal{H}_{ex}$ is the exchange interaction, and $\mathcal{H}'$ includes perturbative terms. Were $\mathcal{H}' = 0$, the ESR spectrum would consist of a sharp resonance at the Larmor frequency ω_0. The effect of perturbative interactions—dipolar and hyperfine—is to create a local field at each spin site that leads to small deviations $\Delta\omega$ from ω_0 ($\Delta\omega \ll \omega_0$). Then the ESR spectrum at infinite temperature is given [6] by

$$I(\theta, \varphi, \omega - \omega_0) \propto \int_{-\infty}^{\infty} \phi(\theta, \varphi, t) \exp[-\mathrm{i}(\omega - \omega_0)t]\, \mathrm{d}t \qquad (1)$$

with

$$\phi(\theta, \varphi, t) \simeq \exp\left(-\frac{1}{\hbar^2}\int_0^t \psi(\theta, \varphi, \tau)(t - \tau)\, \mathrm{d}\tau\right)$$

where

$$\psi(\theta, \varphi, \tau) = \langle\Delta\omega(\tau)\Delta\omega(0)\rangle$$

is the local field correlation function, whose time dependence is governed by $\mathcal{H}_Z + \mathcal{H}_{ex}$. The Zeeman contribution leads to the secular ($\lambda = 0$) and non-secular contributions, resulting in

$$\psi(\theta, \varphi, \tau) = \sum_{\lambda} \gamma^{\lambda}(\theta, \varphi, \tau) \exp(-\mathrm{i}\lambda\omega_0\tau)$$

where $\gamma^{\lambda}(\theta, \varphi, \tau)$ is the exchange-modulated local-field correlation function that verifies $\gamma^{\lambda}(\theta, \varphi, 0) = M_2^{\lambda}(\theta, \varphi)$ (second moment of order λ [11]).

For $\tau > \tau_c$, where τ_c is the time beyond which the local field correlations can be neglected, this gives

$$\phi(\theta, \varphi, \tau) \propto \exp[-(\Gamma(\theta, \varphi, \omega_0) + \mathrm{i}\delta(\theta, \varphi, \omega_0))\tau] \tag{2}$$

where

$$\Gamma(\theta, \varphi, \omega_0) \simeq \frac{1}{\hbar^2}\sum_\lambda \int_0^\infty \gamma^\lambda(\theta, \varphi, \tau)\cos(\lambda\omega_0\tau)\,\mathrm{d}\tau \tag{3a}$$

and

$$\delta(\theta, \varphi, \omega_0) \simeq \frac{1}{\hbar^2}\sum_\lambda \int_0^\infty \gamma^\lambda(\theta, \varphi, \tau)\sin(\lambda\omega_0\tau)\,\mathrm{d}\tau. \tag{3b}$$

Substituting (2) into (1), it can be seen that in a certain range of frequencies near ω_0, the curve will be Lorentzian, centred at $\omega = \omega_0 - \delta(\theta, \varphi, \omega_0)$, with a peak-to-peak linewidth $\Delta B(\theta, \varphi, \omega_0) = (2/\sqrt{3})\Gamma(\theta, \varphi, \omega_0)$. From (3*a*), it may be seen that the linewidth has a secular contribution ($\lambda = 0$) independent of ω_0, while the non-secular contributions are averaged out if $\omega_0 \gg \omega_e$, or have the same weight as the secular ones if $\omega_0 \ll \omega_e$ ('10/3' effect [6, 8, 11]). In both extreme cases, the width and the position of the ESR line will be independent of ω_0. However, frequency-dependent non-secular effects will appear if we perform the ESR experiment at Larmor frequencies $\omega_0 \simeq \omega_e$ [8, 12].

On the other hand, if more than one perturbative mechanism is involved, $\mathcal{H}' = \Sigma_a \mathcal{H}'_a$, the contributions to the linewidth can be considered as additive in the range where the lineshape is Lorentzian [13]. The effects due to the existence of two non equivalent copper sites A and B are included decomposing the Zeeman Hamiltonian in a main term $\mathcal{H}_{Z0}$, proportional to the total spin, plus a small term $\mathcal{H}'_Z$, called 'residual Zeeman', which acts as a perturbation. It is, thus, $\mathcal{H}_{Z0} = \frac{1}{2}\beta(\boldsymbol{S}_A + \boldsymbol{S}_B)\cdot(\mathbf{g}_A + \mathbf{g}_B)\cdot\boldsymbol{B}$, and $\mathcal{H}'_Z = \frac{1}{2}\beta(\boldsymbol{S}_A + \boldsymbol{S}_B)\cdot(\mathbf{g}_A + \mathbf{g}_B)\cdot\boldsymbol{B}$. (Full details can be found in [4].) As $\mathcal{H}'_Z$ is proportional to $B = \hbar\omega_0/g\beta$, the related local field correlation function $\gamma^\lambda_Z(\theta, \varphi, \tau)$ is proportional to ω_0^2:

$$\gamma^\lambda_Z(\theta, \varphi, \tau) = \omega_0^2 m^\lambda_{2Z}(\theta, \varphi)\langle s^+(\tau)s^-\rangle/\langle s^+s^-\rangle$$

where $s^\pm = s^\pm_A - s^\pm_B$, and $m^\lambda_{2Z}(\theta, \varphi)$ is a 'reduced second moment' (the corresponding second moment is $M^\lambda_{2Z}(\theta, \varphi, \omega_0) = \omega_0^2 m^\lambda_{2Z}(\theta, \varphi)$ [13].

Thus, the perturbative Hamiltonian is given by a sum of magnetic dipolar, hyperfine, residual Zeeman and eventually antisymmetric exchange contributions. (Symmetric anisotropic exchange interactions are excluded because they should have a maximum value of $(\Delta g/g)^2 J \simeq 2 \times 10^{-3}$ K) [14].

4. Analysis of the difference in linewidths

If the linewidth given by (3*a*) is calculated for the two microwave frequencies ω_{0X} and ω_{0Q}, and the linewidth at one frequency is subtracted from the other [12], all the secular contributions except the residual Zeeman one will vanish, and the difference in linewidths will be expressed as a function of the non-secular terms ($\lambda \neq 0$) and the residual Zeeman secular contribution $\gamma^0_Z(\theta, \varphi, \tau)$

$$\delta\Gamma(\theta, \varphi, \omega_{0X}, \omega_{0Q}) = \Gamma(\theta, \varphi, \omega_{0X}) - \Gamma(\theta, \varphi, \omega_{0Q})$$

$$= \frac{1}{\hbar^2}\left\{\sum_a \sum_{\lambda_a \neq 0} \int_0^\infty \mathrm{d}\tau\, \gamma^{\lambda_a}_a(\theta, \varphi, \tau)\,[\cos(\lambda_a\omega_{0X}\tau) - \cos(\lambda_a\omega_{0Q}\tau)]\right.$$

$$+ \sum_{\lambda_Z} m_{2Z}^{\lambda_Z}(\theta, \varphi) \int_0^\infty \mathrm{d}\tau \frac{\langle s^+(\tau)s^-\rangle}{\langle s^+s^-\rangle}$$
$$\times \left[\omega_{0X}^2 \cos(\lambda_Z \omega_{0X}\tau) - \omega_{0Q}^2 \cos(\lambda_Z \omega_{0Q}\tau)\right]\Big\} \tag{4}$$

where a = d (dipolar), hf (hyperfine), as (antisymmetric exchange); Z = residual Zeeman interaction and

$$\lambda_a = \begin{cases} 0, \pm 1, -2 & \text{if } a = \mathrm{d} \\ 0, -1 & \text{if } a = \mathrm{hf, as, Z.} \end{cases}$$

To perform the interactions involved in (4), we need to know the time dependence of the local-field correlation functions. A short time expansion [7] enables us to obtain the short-time behaviour of the spin correlation functions, and strong decoupling [12, 15] is assumed when dealing with interactions which are bilinear in their spin operators, as for the dipolar interaction. It is thus obtained that, for short times

$$\gamma_a^{\lambda_a}(\theta, \varphi, \tau) \simeq M_{2a}^{\lambda_a}(\theta, \varphi) \exp(-\tfrac{1}{2}\omega_{ea}^2 \tau^2) \tag{5}$$

where ω_{ea} is the exchange frequency related to the $\boldsymbol{a}$ interaction, given [12, 13] by

$$\omega_{ea} = k_a \, \omega_e$$

with

$$k_a = \begin{cases} 1 & \text{if } a = \mathrm{hf} \\ \sqrt{2} & \text{if } a = \mathrm{d, as} \end{cases} \tag{6a}$$

and

$$\omega_{eZ} = \sqrt{2}\, \omega_{e_{AB}}$$

where

$$\omega_e^2 = \tfrac{1}{2} \sum_j J_{ij}^2 = \omega_{e_{eq}}^2 + \omega_{e_{AB}}^2 \tag{6b}$$

i.e. $\omega_{e_{eq}}^2$ involves the sum over the two equivalent copper neighbours and $\omega_{e_{AB}}^2$ involves the sum over the four non-equivalent copper neighbours. It is seen in (5) that in the short-time regime, the exchange-modulated local-field correlation function can be written as separable functions of time and angle. Regarding the long-time behaviour, it is well known [15] that in low-dimensional systems the long-time regime of the spin correlation functions is strongly modified because of diffusive effects. However, we will neglect these effects when analysing the non-secular contributions, taking into account the fact that the modulation $\cos(\lambda\omega_0\tau)$, with $\lambda \neq 0$, will average out the long-time tail contribution to the integrals of (4). Thus, we will consider only the short-time regime when performing the non-secular integrations. For the residual-Zeeman secular contribution, we will also neglect the long-time tails and consider that the correlation function $\langle s^+(t)s^-\rangle$ decays as in a three-dimensional system. (This approximation will have the effect that the exchange interaction, J', between non-equivalent coppers that is evaluated from the fit will be at a lower limit for its actual value.)

With the above approximations we are able to perform the integrals in (4) to obtain

$$\delta\Gamma(\theta, \varphi, \omega_{0X}, \omega_{0Q}) = \alpha_d^{(1)}(M_{2d}^{(1)}(\theta, \varphi) + M_{2d}^{(-1)}(\theta, \varphi)) + \alpha_d^{(-2)} M_{2d}^{(-2)}(\theta, \varphi)$$
$$+ \alpha_{hf}^{(-1)} M_{2hf}^{(-1)}(\theta, \varphi) + \alpha_Z^{(0)} m_{2Z}^{(0)}(\theta, \varphi) + \alpha_Z^{(-1)} m_{2Z}^{(-1)}(\theta, \varphi). \tag{7}$$

Table 2. Parameters obtained from a least-squares fit of (7) to the linewidth difference data $\delta\Gamma = (\sqrt{3}/2)\delta\Delta B$.

$\alpha_{\mathrm{d}}^{(1)} = (0.22 + 0.03) \times 10^{-3}\ \mathrm{G}^{-1}$	$\alpha_{\mathrm{Z}}^{(0)} = -(3.1 + 0.2) \times 10^{4}\ \mathrm{G}$
$\alpha_{\mathrm{d}}^{(-2)} = (0.00 + 0.07) \times 10^{-3}\ \mathrm{G}^{-1}$	$\alpha_{\mathrm{Z}}^{(-1)} = (0.0 + 0.2) \times 10^{4}\ \mathrm{G}$
$\alpha_{\mathrm{hf}}^{(-1)} = (1.00 + 0.15) \times 10^{-3}\ \mathrm{G}^{-1}$	

The dipolar second moments can be calculated from crystallographic data; $M_{2\mathrm{hf}}^{(-1)}$ is calculated assuming axial symmetry of each copper environment and using the values $A_{\parallel} = 180$ G, $A_{\perp} = 20$ G, resulting from averaged data obtained in several similar dilute systems [16], and the residual-Zeeman contribution is calculated from the g-tensor data [4]. We do not include the antisymmetric exchange contribution in (7), because we do not have enough information to calculate the corresponding second moment, as the chemical paths connecting copper ions are too complex to establish the orientation of the related $\boldsymbol{d}$-vectors [14, 17] in the usual manner. We only know that $M_{2\mathrm{as}}^{(-1)}$ is an angular function varying as a second-order tensor [13], but, in a first approximation, we will consider that its contribution to the difference in linewidths is negligible.

The experimental data on the differences in peak-to-peak linewidth $\delta\Delta B = (2/\sqrt{3})\delta\Gamma$ were least-squares fitted to (7). The coefficients giving the best fit are given in table 2. The function calculated with these values is shown in figure 2, together with the experimental data.

5. Discussion

It may be seen in figure 2 that the difference in linewidths between the data taken at two microwave frequencies is satisfactorily fitted by (7). The resulting values for the coefficients, given in table 2, indicate that non-secular contributions from hyperfine and dipolar interactions play a crucial role in the frequency dependence observed. The signs of the resulting coefficients indicate that we have the expected result that non-secular contributions are more important for the X band, being diminished by modulation at the higher Q-band Larmor frequency. The residual-Zeeman secular interaction also contributes to the frequency dependence, but the minus sign indicates that its contribution is larger at the higher frequency. This is the expected behaviour [4, 5], as the residual-Zeeman second moment depends on ω_0^2. Our results also indicate that the residual-Zeeman non-secular term does not contribute to the frequency dependence.

Calculating the intensity of the second moments, we can extract information about the exchange frequencies from the values of the coefficients in table 2. As the residual Zeeman contribution is negligible for the X band [3], an exchange frequency $\omega_{\mathrm{e}_{\mathrm{AB}}}/2\pi = (10.7 \pm 0.6)$ GHz corresponding to the interaction between non-equivalent coppers can be obtained from the secular residual-Zeeman coefficient of table 2, as in previous works [4, 5]. A separate fit of the Q-band linewidth data leads to the same result. For the analysis of dipolar and hyperfine non-secular terms, replacing the Gaussian short time behaviour in (4), and neglecting intermediate and long-time effects, non-secular coefficients are expressed as a function of the adimensional variable $x_a^\lambda = |\lambda|\omega_{0\mathrm{X}}/)\sqrt{2})\omega_{\mathrm{e}_a}$

$$|\lambda|\alpha_a^\lambda = \left(\frac{\pi}{2}\right)^{1/2} \frac{g\beta}{\hbar} \frac{x_a^\lambda}{\omega_{0\mathrm{X}}} [\exp(-(x_a^\lambda)^2) - \exp(-(\eta x_a^\lambda)^2)] \tag{8}$$

where $\eta = \omega_{0\mathrm{Q}}/\omega_{0\mathrm{X}} = 3.45$, and $g = 2.13$. This function is displayed in figure 3. The

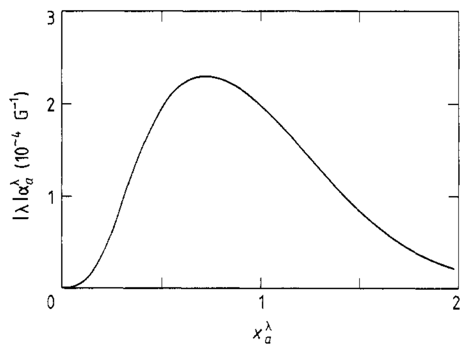

Figure 3. A plot of (8), giving the dependence of the non-secular dipolar and hyperfine coefficients α_a^λ on the adimensional parameter $x_a^\lambda = |\lambda|\omega_{0X}/2\omega_{e_a}$. ω_{0X} corresponds to the X-band Larmor frequency, ω_{e_a} is given by (6*a*) and the values are calculated for the difference between X and Q band linewidth values.

dipolar coefficients of table 2, with the corresponding errors, when interpolated in figure 3, are consistent with a value of the exchange frequency $\omega_e/2\pi = (10 \pm 2)$ GHz. The value of the non-secular hyperfine coefficient, however, exceeds the maximum value allowed by (8), which is $\alpha_{hf}^{(-1)} \langle 0.22 \times 10^{-3}\ G^{-1}$. This fact may be explained if the anti-symmetric exchange contribution is non-negligible, having an angular dependence similar to the hyperfine. If this were the case, as $M_{2as}^{(-1)}$ was not considered explicitly, the hyperfine coefficient resulting from the fit should weight the two interactions, being larger than the value predicted for the interaction only.

Equation (3*b*) predicts that a frequency-dependent linewidth should be accompanied by a frequency-dependent lineshift, leading to a frequency-dependent gyromagnetic factor. This is the case in Cu(L-Phe)$_2$, as may be seen in figure 1(*a*). A detailed fit of the difference in *g*-factors was not performed because the magnitude of the differences is small compared with the experimental error. However, it can be shown [13] that the observed *g*-shifts are in the correct direction and are closely correlated with the angular dependence of the non-secular hyperfine second moment.

On the other hand, non-secular contributions can also explain the frequency dependence of dipolar and hyperfine contributions to the linewidth in Cu(L-Met)$_2$ and Cu(L-Leu)$_2$ [4, 5].

6. Summary and conclusions

We have performed a quantitative analysis of the frequency-dependent effects on the ESR linewidth of an exchange-coupled system, Cu(L-Phe)$_2$. These effects were isolated by subtracting linewidth data obtained at two microwave frequencies, and the different contributions could be identified due to their characteristic angular dependence, given by the corresponding second moments. Using simple hypotheses, the coefficients obtained from a least-squares fit enabled us to estimate the exchange frequency $\omega_{e_{AB}}$ between non-equivalent coppers and the whole exchange frequency ω_e in Cu(L-Phe)$_2$. Comparing the resulting values with (6*b*), we can conclude that the exchange frequency, $\omega_{e_{eq}}$, related to the interaction between equivalent coppers is negligible. Thus, the short-time spin dynamics in Cu(L-Phe)$_2$ are essentially governed by the exchange interaction between non-equivalent coppers. An average interaction, $J' = (0.37 \pm 0.02)$ K, between the four non-equivalent copper neighbours may be estimated using (6*b*). This value, together with the values obtained for two similar complexes [4, 5] is clearly correlated with the Cu–O apical bond lengths involved in the carboxylate bridges [18], reinforcing the hypothesis [5] that these are the main pathways for superexchange between non-equivalent copper atoms.

On the other hand, the goodness of the fit performed demonstrates that non-secular effects must be considered in the analysis of the frequency dependence of the linewidth in $Cu(L\text{-}Phe)_2$, being the only mechanism that can explain the larger linewidths for the X band. For the Q band these effects are averaged out by the higher Larmor frequency.

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