Exchange interactions in bis(L-leucinato)copper(II)

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C A Steren, A M Gennaro, P R Levstein and R Calvo

INTEC, UNL–Consejo Nacional de Investigaciones Científicas y Técnicas, Güemes 3450, 3000 Santa Fe, Argentina

Abstract. In order to evaluate the exchange interaction parameters for interaction between copper ions, we measured the angular variation in the gyromagnetic factor and the linewidth of the single electron paramagnetic resonance line of bis(L-leucinato)Cu(II) single crystals, at 9.7 and 33.6 GHz, and 300 K. We obtain $|J| = 0.17$ K and $|J'| = 0.23$ K for the root mean square values of the exchange interaction of one copper with its six nearest copper neighbours and with its four non-equivalent copper neighbours, respectively. These results are analysed in terms of the chemical pathways for superexchange and compared with those obtained in other similar systems.

Copper amino acid complexes (CACs) provide good model systems for studying the electronic properties of metal ions in proteins, and the magnetic interactions between them. They also have very interesting and novel physical properties which have been studied by electron paramagnetic resonance (EPR) and by magnetic susceptibility [1–4].

Measurements of exchange interactions in CACs allow us to relate their values to the chemical structure, i.e. to the chemical paths connecting the metal ions. Since their magnitudes are $|J| \simeq 0.2$ K, the EPR technique is particularly suitable, allowing us to obtain these small values from data taken at high temperatures.

With these ideas in mind, we performed EPR measurements at the X (9.7 GHz) and Q (33.6 GHz) bands, at 300 K, on oriented single crystals of bis(L-leucinato)Cu(II) (Cu(L-Leu)$_2$). The gyromagnetic factor and the linewidth of the single resonance observed were measured as a function of the orientation of the magnetic field.

In paramagnetic Cu(L-Leu)$_2$, the dipolar, hyperfine and Zeeman interactions within the spin system are modulated by the exchange. Thus, their effects are partially averaged out by the exchange narrowing process [5, 6]. They still contribute, however, producing broadening of the EPR line, with different angular dependences. Thus, from the EPR linewidth data, it is possible to separate the different contributions and to obtain information about the exchange interaction. The gyromagnetic factor of the collapsed resonance is mainly related to the electronic structure of Cu(II) single ions.

The molecular and crystal structure of Cu(L-Leu)$_2$, Cu(H$_2$NCH(CO$_2$)CH$_2$CH-(CH$_3$)$_2$)$_2$, was reported in [7]. It crystallises in the monoclinic P2$_1$, space group with two molecules per unit cell ($Z = 2$), related by a 180° rotation around the $\hat{b}$ axis. Thus, there are two chemically equivalent but magnetically non-equivalent types of copper ions labelled A and B in figure 1. The coppers are arranged in layers parallel to the a–b plane, separated by 14.4 Å. As seen in figure 1, within a layer each copper
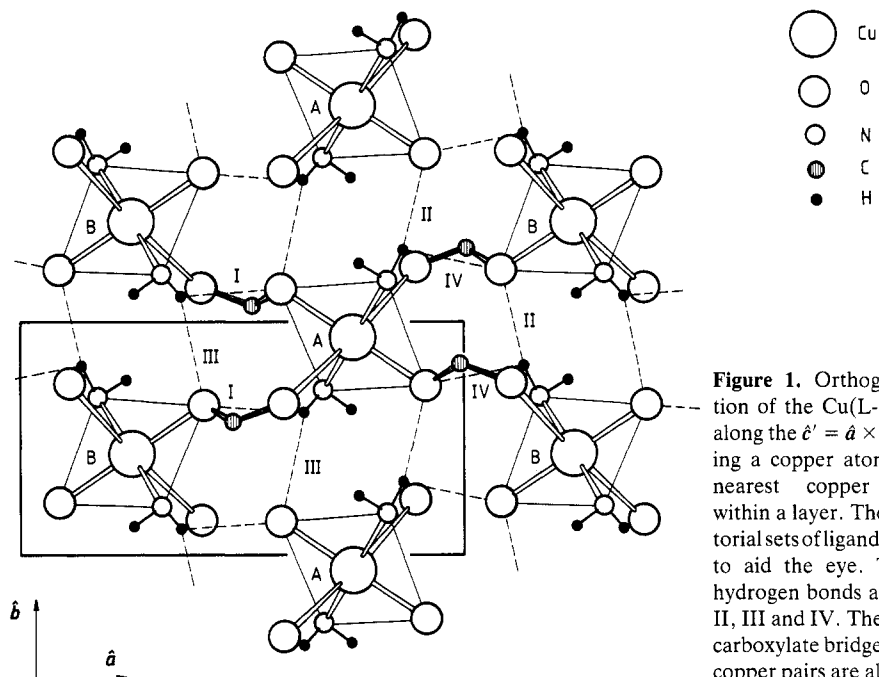
Figure 1. Orthogonal projection of the $Cu(L\text{-}Leu)_2$ crystal along the $\hat{c}' = \hat{a} \times \hat{b}$ axis, showing a copper atom and its six nearest copper neighbours within a layer. The O_2N_2 equatorial sets of ligands are outlined to aid the eye. The possible hydrogen bonds are labelled I, II, III and IV. The two types of carboxylate bridge joining A–B copper pairs are also indicated.

has six nearest copper neighbours in a hexagonal arrangement, at about 5.4 Å. Two copper neighbours are in equivalent sites, and the other four are in rotated sites. The Cu(II) ions are connected to their Cu(II) neighbours by carboxylate and hydrogen bridges. These bridges provide electronic paths for superexchange interactions.

Locally, each copper ion is surrounded by an O_2N_2 equatorial set of ligands at distances of approximately 2.0 Å, which are nearly coplanar with the metal ion. Two apical carboxylic oxygen atoms of adjacent complexes, at an average distance of approximately 2.7 Å, complete a distorted octahedral coordination (see figure 1).

Our EPR data at 9.7 and 33.6 GHz for $Cu(L\text{-}Leu)_2$ single crystals were obtained in three perpendicular planes x–y, z–y and z–x ($xyz \equiv abc'$, $\hat{c}' = \hat{a} \times \hat{b}$), as a function of the orientation of the applied magnetic field B:

$$\hat{h} = B/|B| = (\sin\theta\cos\varphi,\ \sin\theta\sin\varphi,\ \cos\theta).$$

Figures 2 and 3 display the observed angular variations in the squared gyromagnetic factor $g^2(\theta, \varphi)$ at the X band, and the peak-to-peak linewidth $\Delta B(\theta, \varphi)$ at the X and Q bands. The data on the position were fitted to an effective spin Hamiltonian

$$\mathcal{H} = \beta B \cdot \mathbf{g} \cdot S$$

where β is the Bohr magneton, $\mathbf{g}$ the gyromagnetic tensor and S the effective spin operator ($S = \frac{1}{2}$). The values for $g^2(\theta, \varphi) = \hat{h} \cdot \mathbf{g} \cdot \mathbf{g} \cdot \hat{h}$ were used to evaluate the tensor $\mathbf{g}^2$ by the least-squares method. The components of $\mathbf{g}^2$ obtained at each frequency are included in table 1. The full lines in figure 2 are calculated with the tensor obtained using the data at 9.7 GHz. The agreement between experimental and calculated values at this band is as good as that obtained at 33.6 GHz.

The octahedral coordination around the copper ions leads us to assume axial symmetry for the molecular gyromagnetic tensors, with $g_\perp$ in the equatorial plane of ligands,

Table 1. Values of the components of the $\mathbf{g}^2$ tensors, the molecular factors $g_\parallel$ and $g_\perp$, the polar angle θ_M and azimuthal angle φ_M giving the orientation of the molecular axis at one site in the $xyz \equiv abc'$ reference system, and the angle 2α between the molecular axes of the two copper sites, calculated at 9.7 and 33.6 GHz. We also include the values of the A_i parameters obtained by least-squares fits of equation (4) to the linewidth data taken at both frequencies and displayed in figure 3.

Parameter (units)	Value of parameter	
	X band	Q band
g_{xx}^2	4.523 ± 0.001	4.478 ± 0.002
g_{yy}^2	4.525 ± 0.001	4.469 ± 0.002
g_{zz}^2	4.668 ± 0.001	4.640 ± 0.002
$g_{xy}^2 = g_{zy}^2$	0.000 ± 0.001	0.000 ± 0.002
g_{xz}^2	-0.293 ± 0.001	-0.318 ± 0.002
$g_\parallel$	2.265 ± 0.001	2.264 ± 0.002
$g_\perp$	2.072 ± 0.001	2.057 ± 0.002
θ_M (deg)	132 ± 1	133 ± 1
φ_M (deg)	45 ± 1	45 ± 1
2α (deg)	116 ± 1	118 ± 1
A_1 (G)	56 ± 2	20 ± 3
A_2 (G)	14 ± 1	19 ± 1
A_3 (G)	0 ± 80	$(32 \pm 2) \times 10^2$
A_4 (G^{-1})	$(33 \pm 1) \times 10^{-4}$	$(36 \pm 1) \times 10^{-4}$
A_5 (G)	22 ± 1	18 ± 3

and $g_\parallel$ perpendicular to it. Thus, we calculated $g_\parallel$, $g_\perp$, the orientation (θ_M, φ_M) of the molecular axis of one site and the angle 2α between the axes of the two copper sites, using our data and the method in [8]. These values are given in table 1. The molecular orientation (θ_M, φ_M) and 2α are in good agreement with the values $\theta_M = 133.5°$, $\varphi_M = 44.7°$ and $2\alpha = 118.6°$, calculated from the crystallographic data, indicating that axial symmetry is a good assumption for our problem.

The principal values of the molecular gyromagnetic tensor $g_\parallel$ and $g_\perp$, given in table 1, point to a $d_{x^2-y^2}$ ground orbital state for the unpaired electron of the copper ions, as in other CACs [1–4]. The value of $g_\perp$ measured at the Q band is smaller than at the X band and similar to that observed for dilute copper ions with the same coordination in diamagnetic host lattices. We attribute this to contributions from non-secular interactions to the g-shift, which must be taken into account at the X band but are negligible at the Q band.

In order to analyse the linewidth data, we consider the main interactions present in the system:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_E + \mathcal{H}_D + \mathcal{H}_H \tag{1}$$

where $\mathcal{H}_Z$, $\mathcal{H}_E$, $\mathcal{H}_D$ and $\mathcal{H}_H$ are the Zeeman, the Heisenberg exchange, the dipole–dipole and the hyperfine interactions, respectively.

Classical theories of exchange narrowing [6, 9] predict a contribution from $\mathcal{H}_D$ to the linewidth proportional to the second moment of the secular portion of the dipolar interaction. This result is not valid when the spin dynamics has a long-time behaviour characteristic of the diffusive regimen in low-dimensional systems. In two-dimensional systems, the dipole–dipole contribution to the angular dependence of the linewidth is
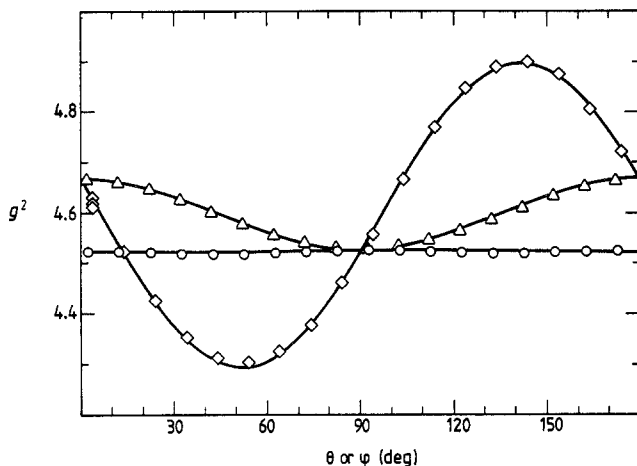
Figure 2. Angular variation in the squared gyromagnetic factor measured at 9.7 GHz, and 300 K, in three orthogonal planes of $Cu(L-Leu)_2$: $\bigcirc$, a–b plane; $\triangle$, b–c' plane; $\diamondsuit$, a–c' plane; ——; curves obtained using the $\mathbf{g}^2$ tensor tabulated in table 1. $\theta = 0°$ corresponds to $\hat{c}'$ for the b–c' and a–c' planes.

given approximately by [10]

$$\Delta B_D(\theta, \varphi) \propto (3 \cos^2 \theta - 1)^2 + \text{constant}. \tag{2}$$

In the absence of exchange, the hyperfine interaction $\mathcal{H}_H$ with the copper nuclear spin $I = \frac{3}{2}$ splits the resonance of each copper site into four. The exchange interaction collapses this structure when $|J| > A$, where A is the hyperfine constant. However, broadening proportional to the second moment $M_H^2(\theta, \varphi)$ of the secular portion of the hyperfine interaction remains [3, 9].

The resonances corresponding to the two copper sites $\alpha = A, B$ in $Cu(L-Leu)_2$ are collapsed owing to the exchange interaction. However, the difference in the g-values can still be observed through the effect on the linewidth when the exchange interaction is not much larger than $|g_A - g_B|\beta|B|$, where $g_\alpha = (\hat{h} \cdot \mathbf{g}_\alpha \cdot \mathbf{g}_\alpha \cdot \hat{h})^{1/2}$, and $\mathbf{g}_\alpha$ is the gyromagnetic tensor corresponding to ions in sites α. As discussed in [4], this contribution is given by

$$\Delta B_Z(\theta, \varphi) = (\nu^2 h^2 / 8|J'|\beta)\{[g_A(\theta, \varphi) - g_B(\theta, \varphi)]^2 / g^3(\theta, \varphi)\}(2\pi/3)^{1/2} \tag{3}$$

where ν is the microwave frequency and $|J'|$ is the root-mean-square value of the exchange parameters of a copper with its four neighbours in inequivalent sites. $|J'|$ involves two exchange parameters between inequivalent coppers owing to the lack of inversion symmetry at copper sites.

A fourth contribution has to be considered to explain the linewidth data. It varies with angle as $(\sin \theta \cos \varphi)^2$ and has been attributed to anti-symmetric exchange [11, 12].

The experimental data for $\Delta B(\theta, \varphi)$ were fitted to a function which considers the four broadening contributions discussed above:

$$\Delta B(\theta, \varphi) = A_1 + A_2(3 \cos^2 \theta - 1)^2 + A_3(g_A - g_B)^2 + A_4 M_H^2(\theta, \varphi)$$

$$+ A_5(\sin \theta \cos \varphi)^2. \tag{4}$$

We have neglected in the A_3 contribution in (4) the small anisotropy introduced by the denominator $g^3(\theta, \varphi)$ in the x–y and z–y planes. The parameters obtained are included

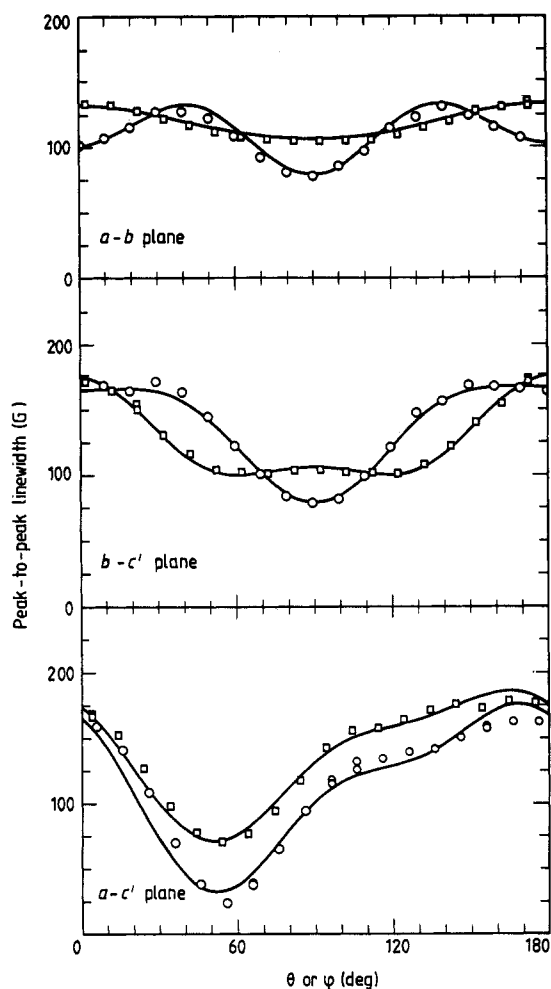**Figure 3.** Angular variations in the peak-to-peak linewidth measured at 9.7 GHz (□) and 33.6 GHz (○), at 300 K, in three orthogonal planes of Cu(L-Leu)$_2$: ———, curves obtained using the parameters calculated from the least-squares fits to equation (4) of the linewidth data at each band and included in table 1.

in table 1. The full lines in figure 3 are obtained with these values and reproduce the experimental points well.

The contribution A_3 varies with frequency as indicated by (3). Consequently, the broadening produced by the difference in g-factors between A and B copper sites allows us to evaluate $|J'| = 0.23$ K for the exchange interaction between nearest non-equivalent copper ions.

The frequency dependence of A_4 is very small and is probably due to non-secular effects. To estimate the exchange interaction which produces the collapse of the four hyperfine lines, we followed the approach in [13, 14], in which the Anderson exchange narrowing model for $I > \frac{1}{2}$ was solved. The asymptotic formulae derived in [13, 14] relate the observed linewidth to M_H^2 and the exchange frequency. Using the Q band value of the coefficient A_4, we obtain $|J| = 0.17$ K for the root mean square magnitude of the exchange interaction of one copper and its six nearest neighbours within a layer.

The A_2 term reflects the importance of the low-dimensional behaviour of the spin dynamics [10]. If one fits the dipole–dipole broadening contribution to our data with a term proportional to the second moment of $\mathcal{H}_D$, as would be expected for three-dimensional spin dynamics, the result is far from satisfactory.

All secular and non-secular mechanisms contribute to A_1. The non-secular contributions would be responsible for the observed reduction in A_1, at the higher frequency.

At this stage, we cannot extract information about the anti-symmetric exchange from the contribution A_5 to (4). We plan to perform measurements in the very similar but centrosymmetric copper (DL-amino acid) compounds, where the anti-symmetric interactions between equivalent copper atoms vanish.

Now, we shall discuss the value obtained for J' in $Cu(L-Leu)_2$ in terms of the chemical paths for superexchange between copper ions and compare this with the results in isomorphous $Cu(L-Met)_2$ [4], in order to reach a more general insight. In both CACs, the usual criteria for the existence of N—H $\cdots$ O hydrogen bridges [15] indicate that those labelled as type IV in figure 1 are out of the limiting condition and can be disregarded. Thus, the only hydrogen bridges connecting inequivalent copper atoms are type I, and they are similar in both systems, considering that the difference between H $\cdots$ O distances at each complex is approximately compensated by the difference in their respective N—H $\cdots$ O angles. However, the magnitude of J' obtained here for $Cu(L-Leu)_2$ is more than twice that of J' obtained in $Cu(L-Met)_2$. This tendency may be correlated with the shorter Cu–O bond lengths of the apical oxygen atoms involved in the carboxylate bridges in $Cu(L-Leu)_2$. This fact leads us to conclude that the carboxylate bridges indicated in figure 1 are important pathways for superexchange between inequivalent copper atoms.

Acknowledgments

References

[1] Newman P R, Imes J L and Cowen J A 1976 Phys. Rev. B 13 4093
[2] Calvo R, Mesa M A, Oliva G, Zukerman-Schpector J, Nascimento O R, Tovar M and Arce R 1984 J. Chem. Phys. 81 4584
[3] Gennaro A M, Levstein P R, Steren C A and Calvo R 1987 Chem. Phys. 111 431
[4] Levstein P R, Steren C A, Gennaro A M and Calvo R 1988 Chem. Phys. 120 449
[5] Kubo R and Tomita K 1954 J. Phys. Soc. Japan 9 888
[6] Anderson P W 1954 J. Phys. Soc. Japan 9 316
[7] Fawcett T G, Ushay M, Rose J P, Lalancette R A, Potenza J A and Schugar H J 1979 Inorg. Chem. 18 327
[8] Abe H and Ono K 1956 J. Phys. Soc. Japan 11 947
    Calvo R and Mesa M A 1983 Phys. Rev. B 28 1244
[9] Abragam A 1961 The Principles of Nuclear Magnetism (Oxford: OUP)
[10] Richards P M and Salamon M B 1974 Phys. Rev. B 9 32
    Richards P M 1975 Local Properties at Phase Transitions (Bologna: Editrice Compositori) p 539
[11] Soos Z G, McGregor K T, Cheung T T and Silverstein A J 1977 Phys. Rev. B 16 3036
[12] Willet R D, Jardine F H, Rouse I, Wong R J, Landee C P and Numata M 1981 Phys. Rev. B 24 5372
[13] Calvo R, Isern H and Mesa M A 1985 Chem. Phys. 100 89
[14] Farach H A, Strother E F and Poole C P Jr 1970 J. Phys. Chem. Solids 31 1491
[15] Olovsson I 1980 Electron and Magnetization Densities in Molecules and Crystals ed. P Becker (New York: Plenum) p 831