

Exchange Interactions in the Copper(II)-*N*-Benzoylglycine (Hippuric Acid) Complex

Ernanni D. Vieira,^a Gianella Facchin,^b Maria H. Torre^b and Antonio J. Costa-Filho^{*,a}

^aDepartamento de Física e Informática, Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos- SP, Brazil

^bCátedra de Química Inorgânica, Universidad de la República, Montevideo, Uruguay

O complexo Cu^{II}-*N*-benzoilglicina provê um sistema conveniente para se estudar interações de troca fracas entre elétrons desemparelhados que são transmitidas por caminhos químicos de interesse biológico. A molécula existe como um dímero onde cada Cu^{II} está coordenado a cinco ligantes, formando uma pirâmide de base quadrada distorcida. O único caminho químico entre íons Cu^{II} magneticamente não-equivalentes envolve 17 átomos diamagnéticos e uma fraca ligação de hidrogênio putativa. Esta interação foi estudada por Ressonância Paramagnética Eletrônica de amostras monocristalinas a 9,5 e 34,5 GHz, tendo sua magnitude sido calculada em 4(1) mK. Esse valor é discutido em termos de valores obtidos para caminhos similares em outros compostos-modelo e proteínas.

The complex Cu^{II}-*N*-benzoilglycine provides a convenient system to study weak exchange interactions between unpaired spins transmitted through a biologically relevant long chemical bridge. The molecule exists as a dimer with each Cu^{II} ion coordinated to five ligands, forming a distorted square-based pyramid. The only chemical connection between magnetically non-equivalent copper ions is a very long path comprising 17 diamagnetic atoms and a weak putative hydrogen bond. This interaction was studied using Electron Paramagnetic Resonance in single-crystal samples at 9.5 and 34.5 GHz and its magnitude was calculated as 4(1) mK. This value is discussed in terms of values obtained for similar paths in other model compounds and in proteins.

Keywords: electron paramagnetic resonance, exchange interactions, model systems

Introduction

Toluene and other volatile organic compounds (VOCs)¹ are widely used as organic solvents in pharmacological, plastic and rubber industries, as well as in various materials such as paints, adhesives and combustion materials.² The exposure to high concentration of toluene and other VOCs causes adverse health effects in nervous system,³ mucous and dermal irritations,⁴ and chromosome aberrations.^{5,6} Toluene is metabolized in human liver microsomes^{7,8} or in rat hepatic microsomes^{9,10} by the hepatic cytochrome P450-mediated mixed function oxidase system to benzyl alcohol, to benzoic acid and finally to hippuric acid, by conjugation with glycine to yield hippuric acid or *N*-benzoilglycine, which is then excreted in urine.¹¹

Copper is a bioessential element with relevant oxidation states.^{12,13} Due to the complexity of metalobiomolecules

and the associated problems, a very useful way of gaining information is examining the behavior of simpler model compounds. The study of ion complexes of copper-amino acids¹⁴⁻²⁶ (or peptides)²⁷⁻³¹ and copper-nucleoside (or related bases)^{32,33} has been a topic of increasing interest in the last few years, mainly due to their relevance in the development of new reagents for biotechnology and medicine.³⁴

N-benzoilglycine is structurally similar to a dipeptide except for the absence of the *N*-terminal group. Due to its high affinity for Cu^{II}, the dimeric complex Cu^{II}-*N*-benzoilglycine could form *in vivo*, especially in cases of increased concentrations of hippuric acid, and could then be used as a means of controlling hippuric acid concentration.

Complexes of *N*-benzoilglycine (hippuric acid) with transition metal ions have already been studied by different physical chemistry techniques.³⁵⁻⁴⁰ In many cases, the copper ions form dimers with identical symmetry around the paramagnetic ions and with a shared ligand mediating

*e-mail: ajcosta@if.sc.usp.br

exchange interaction between those ions. In this case, there is a greater possibility of formation of antiferromagnetically (AFM) coupled dimers, where the singlet ($S = 0$) state is the ground state and the triplet is thermally populated, than the ferromagnetic (FM) interaction at different site symmetries in bimetallic systems,^{41–46} as here reported.

Electron Paramagnetic Resonance (EPR) has been extensively used to study the electronic structure and the local properties of metal ions,⁴⁷ radicals,⁴⁸ and other systems bearing an unpaired electron spin.⁴⁹ EPR enables the evaluation of exchange interactions between coupled metal ions or radicals. In this way, the EPR technique has been used to measure the magnitudes of those interactions, whose nature is related to the electronic structure of the chemical path connecting the copper ions. Their study provides information about pathways that is difficult to obtain when one is dealing with long covalent and noncovalent bonds, whose weak contributions are masked by stronger interactions. On the other hand, the magnitudes of the exchange interactions between unpaired spins are related to the matrix elements for electron transfer between redox centers in proteins,⁵⁰ and thus measurements of exchange couplings give information about electron transfer properties of the path that are difficult to obtain from other sources.^{51–53} In combination with crystal structure data, EPR studies of model compounds allow one to study the magneto-structural correlations needed to characterize properties of weak bonds. This information may be translated to similar chemical paths occurring in macromolecules.

To evaluate the exchange interaction parameters from EPR data, detailed single-crystal measurements are required. The magnitudes of the exchange couplings (J) are calculated from the positions and line widths of the spectra obtained from systems having two or more anisotropic metal ions per unit cell.^{20,21,54–56} Since exchange narrowing, in general, is essentially a temperature-independent phenomenon,^{57–60} the great advantage of these experiments is that exchange interactions having very small magnitudes can be measured at room temperature.

In the present paper we report studies on the magnetic properties of di-(μ -hippurato- O)-bis[*diaqua*(hippurato- O)copper(II)] studied using EPR spectroscopy in single crystal samples at two microwave frequencies, 9 and 34.5 GHz, and at room temperature. The synthesis of a copper complex with *N*-benzoylglycine (hippuric acid), the X-ray structure and the coordination properties of the complex were first studied by Brown *et al.*⁶¹ The EPR results are analyzed using the theories of Anderson,⁵⁷ and Kubo and Tomita⁵⁹ for the exchange narrowing phenomenon. The magnitudes of the exchange interactions between neighbor copper ions are estimated and discussed in terms of bond properties.

Experimental

Synthesis

The complex di-(μ -hippurato- O)-bis[*diaqua*(hippurato- O)copper(II)],¹ or $[\{\text{Cu}(\text{hippurato})_2(\text{H}_2\text{O})_2\}_2]$, was synthesized from the mixture of aqueous solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, 43 mg in 5 mL of water) and sodium hippurate (Sigma, 100 mg in 30 mL of water). The final solution was slowly evaporated at room temperature to yield, after several days, light blue crystals. The composition of the complex was confirmed by elemental analysis, using a Carlo Erba 1108 Elemental Analyser. $[\{\text{Cu}(\text{hippurato})_2(\text{H}_2\text{O})_2\}_2]$ (Found: C, 43.64; H, 5.2; N, 5.74. Calc. for $\text{Cu}[(\text{C}_6\text{H}_5)\text{CONHCH}_2\text{COO}]_2 \cdot 4\text{H}_2\text{O}$, $\text{C}_{18}\text{H}_{24}\text{CuN}_2\text{O}_{10}$: C, 43.95; H, 4.93; N, 5.70%).

EPR measurements

Room temperature EPR spectra of single crystals were recorded at 9.5 (X-band) and 34.5 GHz (Q-band), using a Varian E-109 spectrometer. The angular variation was achieved either by rotating the sample at X-band or rotating the magnet at Q-band. At both frequencies we used 100 kHz magnetic field modulation and $\text{Cr}^{\text{III}}\text{MgO}$ ($g = 1.9797$) as a field marker. The single crystal sample with dimensions (2.5 mm \times 1.0 mm \times 1.0 mm) was fixed with vacuum grease to the xz face of a cubic sample holder made of cleaved KCl crystal, which defined the xyz laboratory coordinate system. The single crystal was then oriented so that the abc crystal system was aligned with the xyz laboratory coordinate system. The sample holder was positioned on a pedestal in the center of the rectangular (X-band) or cylindrical (Q-band) cavities. The magnetic field $\mathbf{B} = B\mathbf{h}$ was then applied in the ab , c^*a and c^*b crystal planes, where $\mathbf{h} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ denotes the direction of the external field in the abc^* axes system. Single crystal spectra were obtained at five degree intervals in those three orthogonal planes. A single resonance line was observed for all orientations of the magnetic field \mathbf{B} in the plane c^*a , while two resonances were observed in the ab and c^*b planes, except for directions close to the crystal axes, where they collapse to a single resonance (Figure 1).

Results and Discussion

Exchange pathways

The compound $\text{Cu}[(\text{C}_6\text{H}_5)\text{CONHCH}_2\text{COO}]_2 \cdot 4\text{H}_2\text{O}$ reported by Brown *et al.*⁶¹ crystallizes in the monoclinic space group $P2_1/c$, with $Z = 2$, four ions Cu^{II} ions per unit

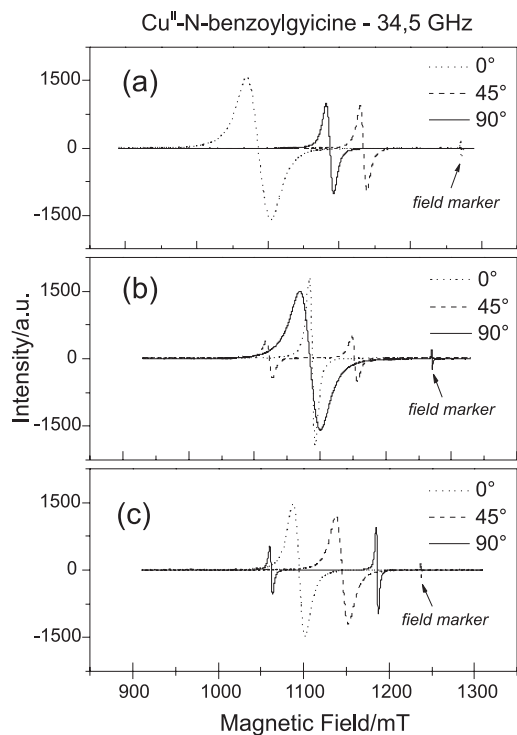


Figure 1. EPR spectra at Q-band (34.5 GHz) of the compound Cu^{II} -*N*-benzoylglycine, showing the phenomenon of collapse and line narrowing by exchange in the *ab* (b) and *c*b* (c) crystal planes. The *c*a* (a) plane presents only one line as a consequence of the symmetry of the spatial group $P2_1/c$.

cell, $a = 7.253(1) \text{ \AA}$, $b = 40.169(3) \text{ \AA}$, $c = 7.466(1) \text{ \AA}$, and $\beta = 102.81(1)^\circ$. The molecule exists as a dimer with each Cu^{II} ion coordinated to five ligands forming a distorted [4 + 1] square-based pyramid. The coordination sphere of each Cu^{II} ion is constituted by an oxygen atom from a hippurate ion (O_{14}), two water molecules (W_1 and W_2), and two other hippurate ions, whose oxygen atoms (O_{11} and O_{11^*}) act as μ -oxi bridges in the dimer (Figure 2).

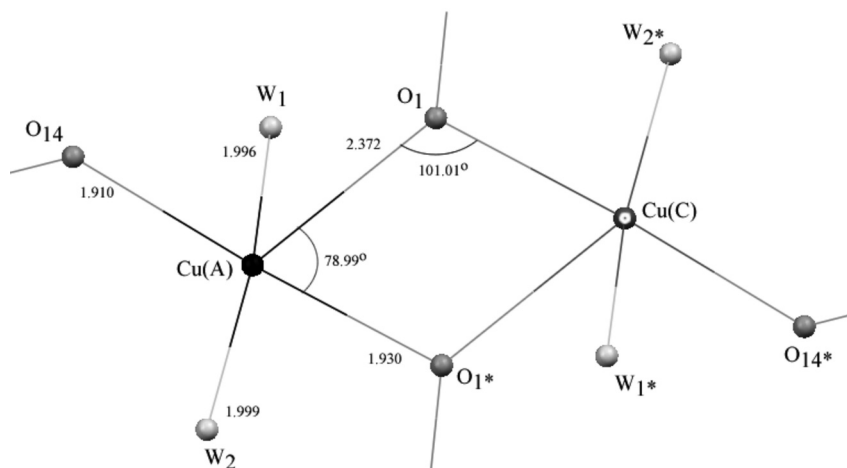


Figure 2. Schematic drawing of the copper coordination sphere with distances (in Angstroms) and angles indicated.

The $P2_1/c$ symmetry operations relate the four Cu^{II} ions as follows: from $\text{Cu}(\text{A}) = (x; y; z)$, the other three copper sites are $\text{Cu}(\text{B}) = (-x; 1/2+y; 1/2-z)$, $\text{Cu}(\text{C}) = (-x; -y; -z)$, and $\text{Cu}(\text{D}) = (x, 1/2-y; 1/2+z)$. The crystal packing shows two molecular chains: *chain 1* is formed by molecules containing copper ions $\text{Cu}(\text{A})$ and $\text{Cu}(\text{C})$ and *chain 2* is composed by molecules with $\text{Cu}(\text{B})$ and $\text{Cu}(\text{D})$, each forming a helix-like structure along the crystalline axes *a* and *c*, respectively.

Due to the chain structure observed for the Cu^{II} -*N*-benzoylglycine, the chemical connections between Cu^{II} ions are better discussed when presented as *intra* and *inter-chain* connections. Many chemical paths can be identified as *intra-chain* connections and all involve magnetically equivalent Cu^{II} sites. The contacts between $\text{Cu}(\text{A})$ and $\text{Cu}(\text{C})$ (or $\text{Cu}(\text{B})$ and $\text{Cu}(\text{D})$) are supported by two μ -oxi bridges (Figure 2). Other possible paths that connect the same type of ion in different molecules (for example, $\text{Cu}(\text{A})$ in one molecule and $\text{Cu}(\text{A})$ in a symmetry-related molecule) are mediated by several weak hydrogen bonds. These contacts along with the strong μ -oxi bridges couple magnetically equivalent copper ions, which makes the determination of the associated coupling magnitudes not feasible from EPR experiments.

As for inter-chain contacts, the only significant connection found in the structure comprises a very unusual path involving hydrogen $\text{H}_{(2)}$ of the aromatic ring of one molecule of the hippuric acid in chain 1 and the carbon $\text{C}_{(3)}$ of the aromatic ring of the hippuric acid of chain 2 (Figure 3). The distance $d_{[\text{C}_{(3)}-\text{H}_{(2)}]}$ is 3.550 \AA and the angle between atoms $\text{C}_{(3)}-\text{H}_{(2)}-\text{C}_{(11)}$ is 103.70° . This connection is long, involving 17 diamagnetic atoms with total bond distances $d_{[\text{Cu}(\text{A})-\text{Cu}(\text{B})]} = 28.332 \text{ \AA}$ and $d_{[\text{Cu}(\text{A})-\text{Cu}(\text{D})]} = 27.890 \text{ \AA}$. The spatial separation between ions is $d_{[\text{Cu}(\text{A})-\text{Cu}(\text{B})]} = 20.173 \text{ \AA}$ and $d_{[\text{Cu}(\text{B})-\text{Cu}(\text{D})]} = 19.671 \text{ \AA}$. This chemical

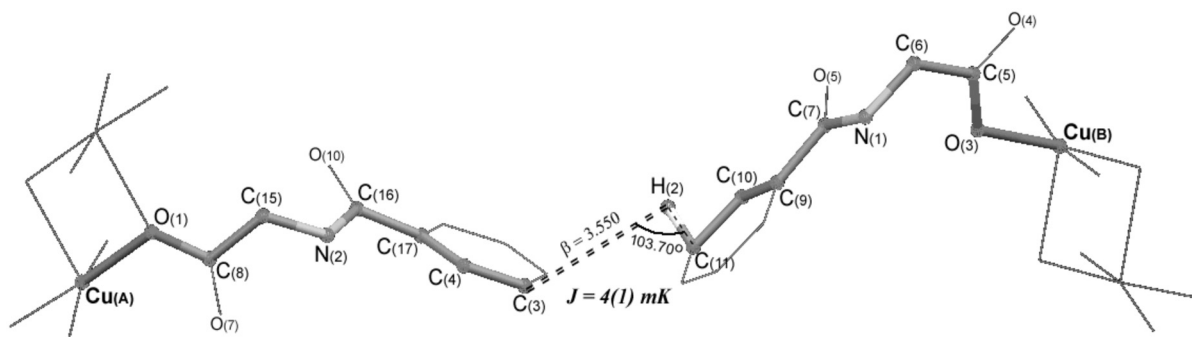


Figure 3. Two neighbor copper ions separated by path containing the hydrogen bond discussed in the text are displayed. The distance and the angle of the putative hydrogen bond between molecules are given in Angstroms (Å) and degrees (°), respectively.

path has extremely weak character, since it encompasses long contacts through weakly electronegative atoms. One possible explanation for the establishment of such path would be the existence of a water molecule in the crystal structure which has not been detected when the structure was first determined.

EPR results

A single resonance line was observed for all orientations of the magnetic field \mathbf{B} in the plane c^*a , while two resonances were observed in the ab and c^*b planes, except for directions close to the crystal axes, where they collapse to a single resonance (Figure 1). The positions and peak-to-peak line widths (ΔB_{pp}) of the single resonance for the c^*a plane, or the two resonances in some orientations of the ab and c^*b planes, were obtained from least-squares fits of the field derivative of one or two Lorentzian lines to the observed signal (Figure 1). The angular variation of the line positions and line widths calculated from the EPR spectra are shown in Figures 4 and 5.

The data in Figures 4 and 5 can be analyzed in terms of a spin Hamiltonian written as^{21,23,28}

$$H = H_z + H_{ex} = \sum_i \sum_{\alpha} \mu_B \vec{B} \cdot \vec{g}_{i\alpha} \vec{S}_{i\alpha} - \sum_{i\alpha, j\beta} J_{i\alpha, j\beta} \vec{S}_{i\alpha} \cdot \vec{S}_{j\beta} \quad (1),$$

where H_z and H_{ex} are the contributions appearing from the Zeeman and exchange interactions, $S_{i\alpha}$ is the spin operator corresponding to a copper ion in the ($\alpha = A, B, C,$ or D) position of the i th unit cell ($S = 1/2$), and μ_B is the Bohr magneton. As described in the previous section, the compound $\text{Cu}^{\text{II}}\text{-N-Benzoylglycine}$ belongs to space group $P2_1/c$ with two dimer units per unit cell. The distances between copper ions in the crystallographic structures are greater than 7.5 \AA , and thus dipole-dipole interactions were disregarded in equation 1³¹. The g_{α} are the symmetry-related molecular g -tensors associated to each copper ion in the

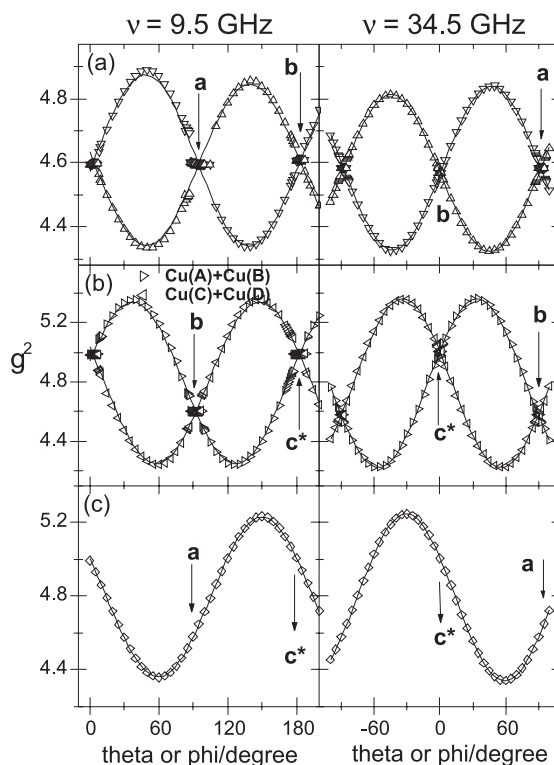


Figure 4. Angular variation of the molecular $g^2_{\alpha}(\theta, \phi)$ tensors of each copper site (solid line) in three crystal planes of single crystals of $\text{Cu}^{\text{II}}\text{-N-Benzoylglycine}$. Open triangles give the experimental data at 9.5 and 34.5 GHz. The solid lines were obtained with the components of g^2 given in Table 1. The data in the c^*a plane (c) display a single resonance line for all orientations of the magnetic field \mathbf{B} , whereas ab (a) and c^*b (b) planes display the collapse of the EPR lines near the crystal axes.

sites defined before. Thus, $g_A \equiv g_B$ and $g_C \equiv g_D$, with g_A, g_C and g_B and g_D related by a C_2 rotation around the \mathbf{b} axis. Considering only exchange interactions between nearest neighbor copper ions and the symmetry conditions relating the exchange interaction parameters $J_{i\alpha, j\beta}$ in equation 1, only few different parameters contribute, which are discussed below in terms of the crystal structure of the compound.

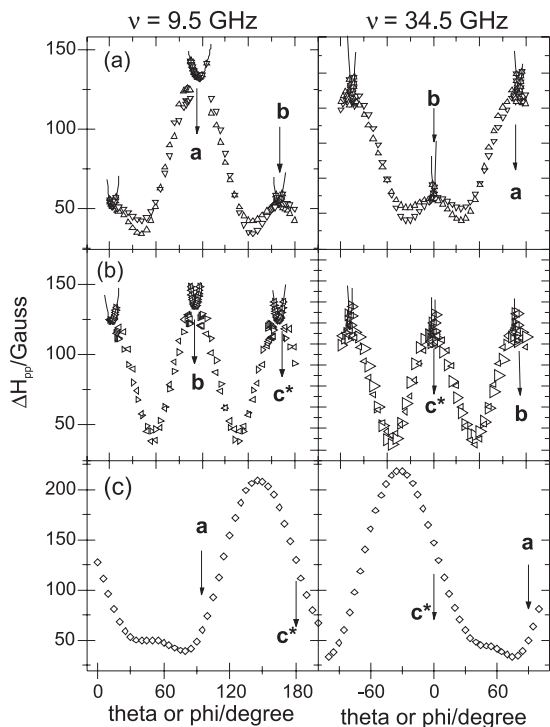


Figure 5. Angular variation of the peak to peak EPR line width observed at 9.5 and 34.5 GHz for a magnetic field applied in the three crystalline planes *ab* (a), *c*b* (b), and *c*a* (c) of the single crystal sample Cu^{II}-*N*-benzoylglycine. The solid lines are obtained with equation (9) and parameters are included in Table 1.

Based on the previous discussion, the Zeeman and exchange interactions can be written in this case as⁵⁵

$$H_z = \mu_B \sum_i \vec{B} \cdot (\vec{g}_A \vec{S}_{iA} + \vec{g}_B \vec{S}_{iB} + \vec{g}_C \vec{S}_{iC} + \vec{g}_D \vec{S}_{iD}) + \mu_B (\vec{S} \vec{g} \vec{B}) + \mu_B \sum_u \vec{B} \cdot \vec{G}_u \vec{s}_u \quad (2)$$

$$H_{ex} = J_{AA} \sum_{i,m} \vec{S}_{iA} \vec{S}_{m\alpha} + J_{AB} \sum_i (\vec{S}_{iA} \vec{S}_{iB} + \vec{S}_{iC} \vec{S}_{iD}) + J_{AD} \sum_i (\vec{S}_{iA} \vec{S}_{iD} + \vec{S}_{iB} \vec{S}_{iC}) \quad (3)$$

where $\vec{S} = \sum \vec{S}_i$ and $\vec{g} = \sum \vec{g}_i$, and the exchange paths associated with the exchange parameters J_{AA} , J_{AB} , and J_{AD} were described above. The sum over m in the first term is over the nearest neighbor copper ions in cell i . Since $g_A = g_B$ and $g_C = g_D$ in equation 2, the contributions to H_{ex} proportional to J_{AA} and J_{AB} in equation 3 do not produce any effect on the spectra.

The angular variation of the g^2 -tensor (Figure 4) shows that, for some orientations of the magnetic field, two resonance lines are resolved in the EPR spectra, which in turn collapse for directions around the crystal axes. This scheme can be rationalized in terms of a competition

between the residual Zeeman interaction, the difference in Zeeman energy of two magnetically non-equivalent Cu^{II} sites, and the respective exchange interaction. At some orientations, J_{ex} is greater than the residual Zeeman interaction and then a single line is observed. This situation allows us to use a perturbation approach and divide the contributions to the Spin Hamiltonian in equation 1 in H_0 and H_1 , where H_1 represents the weaker interactions perturbing the term H_0 . Two resonance regimes arise (split and collapsed regimes), whose differences rely on the interplay between exchange and residual Zeeman contributions to H_1 .

Split resonance regime

In the split resonances regime, where two resonance lines are observed (planes *ab* and *c*b*; see Figures 4 and 5), the Hamiltonians H_0 and H_1 may be written as

$$H_0 = H_z \quad (4)$$

$$H_1 = H_{ex} \quad (5)$$

Each one of the lines observed in the planes *ab* and *c*b* corresponds to a magnetically non-equivalent Cu^{II} site (Cu(A) or Cu(B)). The molecular g_α -tensor is obtained directly from the data in Figure 5 in the regions where the lines are well-resolved, without the necessity of the use of decomposition methods. A least-squares fitting of the experimental data in those regions, for all orientations in the *c*a* plane against the function $\vec{g}^2 = \hat{h} \cdot \vec{g} \cdot \vec{g} \cdot \hat{h}$, leads to the components of the g_α tensors given in Table 1. These results are used to draw the solid lines in Figure 4.

Collapsed resonances regime

In the collapsed resonances regime (*ab* and *c*b* planes near the crystal axes), the unperturbed Hamiltonian H_0 should be written as

$$H_0 = \mu_B \vec{B} \vec{g} \vec{S} + H_{ex} \quad (6)$$

where $S = \sum \vec{S}_{i\alpha}$ is the total spin of the system and $g = (g_A + g_B + g_C + g_D)/4$ is the average g tensor. The exchange interaction H_{ex} commutes with the total spin S , and thus H_0 gives rise to a single EPR line at the average g factor. The perturbation can be written in this case as⁵⁵

$$H_1 = \mu_B \sum_u \vec{B} \cdot \vec{G}_u \vec{s}_u \quad (7)$$

and the line broadening is⁶²

Table 1. Values of the components of the crystal and molecular \vec{g}^2 tensor obtained by least-squares analyses of the data at each microwave frequency. $(g^2)_1$, $(g^2)_2$, and $(g^2)_3$ and \vec{v}_1 , \vec{v}_2 and \vec{v}_3 are the eigenvalues and eigenvectors of the \vec{g}^2 tensor in *abc** coordinate system^(a)

	9.5 GHz	34.5 GHz
g_{xx}^2	4.578(1)	4.578(1)
g_{yy}^2	4.578(4)	4.576(2)
g_{zz}^2	5.007(4)	5.006(4)
g_{xy}^2	$\pm 0.259(6)$	$\pm 0.250(2)$
g_{zx}^2	$\mp 0.511(6)$	$\mp 0.526(2)$
g_{zy}^2	$-0.387(1)$	$-0.399(5)$
$(g^2)_1$	4.238(7)	4.221(3)
$(g^2)_2$	4.359(3)	4.358(3)
$(g^2)_3$	5.566(6)	5.581(5)
\vec{v}_1	(∓ 0.01485 ; 0.83602; ± 0.054849)	(± 0.09356 ; 0.80413; ± 0.58704)
\vec{v}_2	(-0.90443 ; ± 0.22268 ; -0.36390)	(0.90016; ± 0.32025 ; -0.29521)
\vec{v}_3	(-0.42637 ; ∓ 0.50148 ; 0.75281)	(-0.42539 ; ∓ 0.50081 ; 0.05381)
$g_{\parallel} = g_{Cu-O_1}$	2.3593(5)	2.3624(9)
$g_{O_{14}-O_1}$	2.0877(3)	2.0875(8)
$g_{W_1-W_2}$	2.0586(8)	2.0545(7)

^(a)The values of $g_{O_{14}-O_1}$, $g_{W_1-W_2}$ and $g_{\parallel} = g_{Cu-O_1}$ represent the molecular g value for each compound in oxygen-oxygen, water-water, and parallel directions, respectively.

$$\Delta B_{pp}(\theta, \phi) = \sqrt{\frac{2\pi}{3}} \sum_{u=1}^3 \frac{\omega_0^2 \hbar}{g \mu_B \omega_{ex}} \frac{\hat{h} \vec{g} \vec{G}_u \hat{h}}{g^2(\theta, \phi)} + \Delta B_{pp}(0) \quad (8)$$

where G_u accounts for the differences among the four molecular g factors. $\Delta B_{pp}(0)$ is a residual line width that considers the small line width observed for the magnetic field along the crystal axes (Figure 5). Due to the space symmetry of the compound, and neglecting the interaction between A and C type copper electron spins, the sum over u contains a single term^{28,67}

$$\frac{\hat{h} \vec{g} \vec{G}_u \hat{h}}{g^2(\theta, \phi)} \approx \left[\frac{g_A(\theta, \phi) - g_D(\theta, \phi)}{2} \right]^2 = g_{xy}^2 \sin^2 \phi \cos^2 \phi \quad (9)$$

A least-squares fitting of the line width data against the function defined in equation 9 for the regions around the crystal axes in the *ab* and *c***b* planes of the compound was performed. The values of the off-diagonal components of the molecular g tensors g_A and g_D presented in Table 1 were used in this calculation. The results of these fittings are shown as solid lines in Figure 5. These values and equation 9 were used to obtain the exchange frequencies and the values of the exchange coupling parameters

$$|J_{AD}/k| = 4(1)mK \quad (10)$$

The magnitude of J_{AD} (4 mK, *ca.* 0.0028 cm⁻¹) is very weak, as expected from the exchange pathway analysis

described above. Similar magnitudes of exchange coupling between copper ions have been found in several complexes. In dichlorobis(1-phenyl-3,5-dimethylpyrazole)copper(II), an exchange coupling of 0.00386 cm⁻¹ (*ca.* 5.5 mK) was found, mediated by a long path (bond distance 13.60 Å) constituted by the pyrazole ring and a hydrogen-halogen bond C–H...Cl⁶⁴. In the complex Cu(Gly)₂·H₂O, Hoffman *et al.*⁵⁴ determined an exchange interaction of 0.004 cm⁻¹ (*ca.* 5.7 mK) between magnetically non-equivalent copper ions connected through a hydrogen bond between a coordinated water molecule and a glycine oxygen atom. More recently, Santana *et al.*⁶⁵ calculated the coupling magnitude between copper ions in the compound Cu^{II}(L-arginine)₂(SO₄)(H₂O)₆, finding a weak coupling of 9 mK assigned to a long path with 12 atoms (total bond distance 19.789 Å) and two hydrogen bonds. Furthermore, in the complex aqua(glycyl-L-tryptophanate)-copper(II) dehydrate, an exchange coupling of 3 mK was found and also assigned to a long path with 10 diamagnetic atoms, including a moderate hydrogen bond (total bond distance 16.69 Å). All these model systems are very nicely related to the biological electron transfer system in the bacterial photosynthetic reaction center protein of *Rhodobacter sphaeroides*, where the coupling between the two quinone acceptors at 17.3 Å is 3.8 mK.⁶⁶ Following the classification proposed by Vieira *et al.*,³¹ the exchange coupling determined in the present work would be in their group III,

which includes long paths with more than 10 diamagnetic atoms and magnitudes of the order of few milliKelvin.

Conclusions

In this article we studied the magnetic properties of the Cu^{II}-*N*-benzoylglycine compound, whose interest is associated with its toxicology or ecotoxicology. The EPR technique, along with X-ray diffraction data, supplies information on the possible chemical path and the magnetic interactions established in model metal-ligand complexes. From the analysis of the experimental data, it is possible to calculate the coupling constants between the paramagnetic sites. These couplings usually present very weak magnitudes and are thought to model biologically-relevant interactions. One can readily see that room-temperature EPR measurements can thus offer unique possibilities of evaluating very small magnitude interactions, which would be directly detected by other experimental techniques only by means of very low temperature measurements.

In the Cu^{II}-*N*-benzoylglycine complex, the copper coordination sphere in each site is a slightly distorted square-based pyramid with values of $g_{\parallel} > g_{\perp}$, which indicates that the ground-state orbital of the copper ions is essentially a $d_{x^2-y^2}$ state. The values obtained from the data at 34.5 GHz in the Table 1, $g_{\parallel} = 2.3624(9)$, $g_{O(14)-O(1)} = 2.0875(8)$, $g_{W(1)-W(2)} = 2.0545(7)$, indicate that the electron ground-state orbital is in the plane containing the copper ion and the hippurato oxygen and water ligands. The only interactions that we can quantify using the EPR technique are the inter-chain contacts that relate copper ions in the two different chains observed in the crystal structure. The evaluated magnitude $|J/k|$ is 4(1) mK. This low value of $|J/k|$ agrees well with the described chemical path discussed in the text.

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