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Note

Magnetic interactions in aqua(L-aspartato)-(2,2′-bipyridine)copper(II) trihydrate

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Abstract

We report magnetic susceptibility measurements in polycrystalline samples and EPR measurements at X-band in single crystal samples of the ternary complex of copper with aspartic acid and bipyridine, aqua(L-aspartato)(2,2′-bipyridine)copper(II) trihydrate, Cu(asp)bpy. This compound exhibits a layered structure for the copper ions. Within each layer, these ions are connected by a chemical path that involves a carboxylate bridge and a hydrogen bond, and by the stacking of the aromatic rings of the bipyridyl ligands. They provide the pathways for magnetic superexchange. Magnetic susceptibility data indicate a weakly ferromagnetic Curie–Weiss behavior in the studied temperature range (2–300 K), and molecular field theory gives $J/k_B = 0.12(4)$ K for the mean value of the exchange parameter between copper ions. We observed a single exchange collapsed EPR line in Cu(asp)bpy for any orientation of the magnetic field. The g tensor is nearly diagonal and axially symmetric, in agreement with the crystal structure. The linewidth $\Delta B_{pp}(\theta,\phi)$ exhibits a behavior characteristic of a two-dimensional system, which originates in the layered structure of Cu(asp)bpy. From the EPR data we estimate $|J| = |(J_C + J_B)/2| \approx |J_C| \approx |J_B| = 0.20(3)$ K, where J_C is the exchange parameter associated with the chemical path involving the carboxylate bridge and the hydrogen bond, and J_B is that associated with the stacking of the bipyridyl ligands. There is a reasonable agreement between the exchange parameters obtained from susceptibility and EPR measurements. The J_B value indicates that the stacking of the aromatic rings may act as a sizeable exchange interaction path.

Keywords: Magnetism; Crystal structures; Copper complexes; L-Aspartato complexes; Bidentate ligand complexes

1. Introduction

Studies of the magnetic interactions in the copper complexes of the amino acids L-glutamic and L-aspartic have been reported recently [1,2]. In both compounds, the side chains of the amino acids are in highly extended configurations [2,3], and they form polymeric compounds with chains of the type –aa–Cu–aa–Cu–aa (aa = L-glutamic (glu) or L-aspartic (asp)). These studies allowed evaluation of the exchange interaction parameters $|J/k_B| = 0.19(2)$ K and $J/k_B = -5.3(2)$ K for copper ions connected through the σ-skeleton of glutamic and aspartic acid molecules. The ternary copper complexes of glu and asp with the aromatic amines (ar) imidazole (im), bipyridine (bpy) and phenanthroline (phen) (Cu(aa)ar), have been studied in the solid state [4–7]. In all these compounds, the side chains of the glu molecules are in extended configurations. Cu(glu)im and Cu(glu)bpy are polymeric compounds, while Cu(glu)phen is a monomeric compound [6]. The side chain of the asp molecule adopts an extended configuration in Cu(asp)im and Cu(asp)bpy. Cu(asp)im [4] is a polymeric compound, while Cu(asp)bpy [5] is a monomeric compound. In the structure of Cu(asp)phen reported by Antolini et al. [7], the asp molecule forms a monomeric compound adopting the configuration of a tridentate ligand toward the same metal ion. Recently, we have synthesized and solved the structure of a different ternary copper complex with asp and phen

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having both monomeric and polymeric structures in the same lattice [8]. Thus, the aromatic amines alter the polymeric structures of Cu(glu) and Cu(asp), adding interest to the study of the ternary compounds. An interesting characteristic of the ternary copper complexes described above (except Cu(glu)im), is the stacking of the rings of the aromatic amines. This is a 'non-covalent' interaction commonly classified within hydrophobic interactions. The importance of the hydrophobic interactions in metallic complexes of organic molecules in solution has been studied by Fisher and Sigel [9], and more recently, in solution and in the solid state by Sugimori et al. [10]. Fisher and Sigel pointed out that these interactions may favor the formation of these complexes, and that they are responsible for the creation of distinct structures in biological compounds. Hydrophobic interactions also contribute to the stabilization of the crystal packing of the mixed complexes Cu(aa)ar in the solid state [4–7].

The magnetic properties of these compounds, as well as the properties of the hydrophobic interactions as exchange interaction paths between metal ions, have received much less attention. This may be a consequence of the related difficulties in the measurement of the small magnitudes of the exchange associated with these chemical paths. Here we report on progress made in this direction. Magnetic susceptibility measurements in powdered samples, and EPR measurements at X-band in single crystals of the ternary complex of copper with aspartic acid and bipyridine, a compound whose structure has been reported by Antolini et al. [5], are presented and discussed. It exhibits a layered structure for the copper ions. Within each layer the copper ions are connected by a chemical path that involves a carboxylate bridge plus a hydrogen bond, and by the aromatic ring stacking of the bipyridyl ligands. Our EPR results in Cu(asp)bpy indicate a two-dimensional magnetic behavior, and show the ability of a hydrophobic interaction to act as an exchange interaction path between copper ion pairs.

2. Experimental

2.1. Materials

The compound Cu(asp)bpy was prepared by mixing solid Cu(asp)$(H_2O)_2$ suspended in hot water with a solution of the aromatic amine in methanol. The resulting blue solution was left to stand several days, yielding prismatic blue crystals. The prisms are elongated along the direction of the c axis and have (110) lateral faces. The axes a and b of the single crystal samples were identified by measuring the angles between the lateral faces with a goniometric microscope and by X-ray measurements.

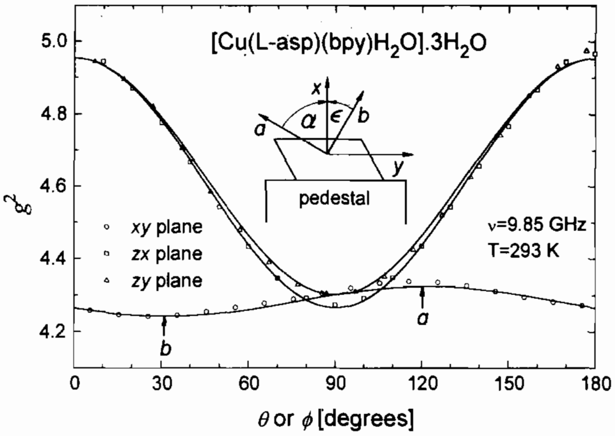

Fig. 1. Angular variation of $g^2(\theta,\phi)$ at 9.85 GHz for the magnetic field applied in the $xy=ab$, zy and zx crystalline planes of the single crystal of Cu(asp)bpy. The solid lines are obtained with the components of g^2 included in Table 1. The inset shows the mounting of a sample of Cu(asp)bpy on the measurement pedestal, indicating the positions of the crystalline axes a and b in the xyz system axes holder.

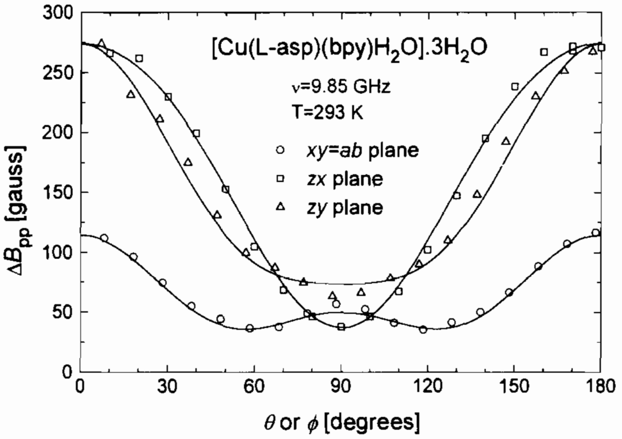

Fig. 2. Angular variation of the peak-to-peak EPR linewidth observed at 9.85 GHz, for the magnetic field applied in the three crystalline planes $xy=ab$, zx and zy of a single crystal sample of Cu(asp)bpy. The solid lines are obtained with Eq. (4) and the parameters included in Table 1.

2.2. Magnetic measurements

Magnetic susceptibility (χ) measurements in powdered samples were performed using an SHE, Corp. VTS 906 variable temperature magnetometer at a field of 1 kG, in the range between 2 K and room temperature. The data obtained were corrected for the diamagnetic contribution using Pascal constants. EPR data in single crystals were obtained at 9.85 GHz and room temperature with a Bruker ER-200 EPR spectrometer using a 12 in. rotating magnet, and a Bruker cylindrical cavity with 100 KHz field modulation. To orient the single crystal samples, a (110) crystal face was glued to a cleaved KCl cubic holder which defines a set x, y, z of orthogonal axes. The c axis is along the z axis of the holder, and according to the structural data, a and b form angles $\alpha=62.8°$ and $\epsilon=27.2°$ with the x axis, respectively (see inset in Fig. 1). The sample holder was positioned in a horizontal plane at the top of a pedestal in the center of the microwave cavity, and the magnetic field B was rotated in the xy, zx and zy planes of the samples. A single EPR line was observed for Cu(asp)bpy at any magnetic field orientation. The values for the squared g factor $g^2(\theta,\phi)$ and the peak to peak linewidth $\Delta B_{pp}(\theta,\phi)$ measured at X-band are displayed in Figs. 1 and 2, respectively.

3. Results and discussion

3.1. Crystal structure of Cu(asp)bpy

The structure of Cu(asp)bp is orthorhombic, space group $P2_12_12_1$, $Z=4$, and lattice parameters $a=21.978$, $b=11.275$ and $c=6.841$ Å [5]. The four symmetry related molecules in the unit cell are labeled as I, II, III and IV. The arrangement of the ligands around Cu(II) (see Fig. 3(a)) is five-coordinated distorted square pyramidal. In the equatorial plane there are two nitrogens from the bpy ligand (N1, N2), and the oxygen and the nitrogen of the amino acid group of the asp molecule (O1, N3). The apical position is occupied by an oxygen from a water molecule (O1w) at 2.368 Å. A sixth octahedral position occupied by O2 from a neighboring asp molecule is not considered as a structural bond, due to the relatively long length of the Cu–O2 bond (3.019 Å) [5]. The structural results [5] indicate that the normals to the planes of the equatorial ligands to the four copper ions in the unit cell, are approximately contained in the ca crystal plane (see Fig. 3(b)). Then, considering the symmetry operations of the space group $P2_12_12_1$, the orientations of the normals corresponding to sites I and IV, and II and III are almost collinear (Fig. 3(b)). Copper ions at sites I and II, as well as those at sites III and IV, are respectively in two symmetry-related layers separated by about 11.5 Å, parallel to the cb crystal plane. Within each layer, copper ions at 5.95 Å are connected from an apical position to an equatorial position, by a chemical path of five atoms involving a carboxylate bridge plus a hydrogen bond (Fig. 4). A more direct interaction mediated by carboxylate bridges bridging the copper ions at 5.95 Å is neglected as a chemical path due to the long length of the Cu–O2 bond (3.019 Å). Copper ions at 7.67 Å are connected from an equatorial position to an equatorial position by the aromatic ring stacking of the bpy ligands (Fig. 4). Copper ions in different layers are very weakly connected by paths involving double hydrogen bonds, which are not discussed here.

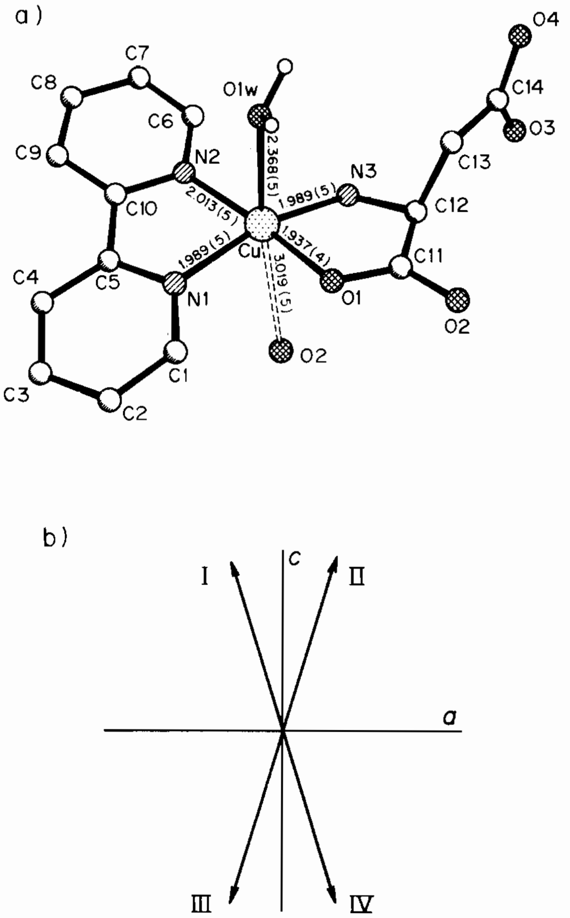

Fig. 3. (a) Coordination around copper ions in Cu(asp)bpy from Ref. [5]; bond distances are given in Å. (b) Normals to the planes of ligands for the four copper ions in the unit cell.

3.2. Magnetic susceptibility data

A Curie–Weiss behavior $\chi(T)=C_m/(T-\theta_c)$ was observed for Cu(asp)bpy in the whole studied temperature range. A least-squares fit of the data between 16 and 100 K gave $C_m=0.398(1)$ emu-K/mol and a ferromagnetic Curie temperature $\theta_c=0.24(4)$ K. The small value for θ_c reflects the quasi-molecular characteristic of Cu(asp)bpy, and indicates that the copper ions are connected by weak exchange couplings. We estimated a mean value $J/k_B=0.12(4)$ K for the exchange parameter

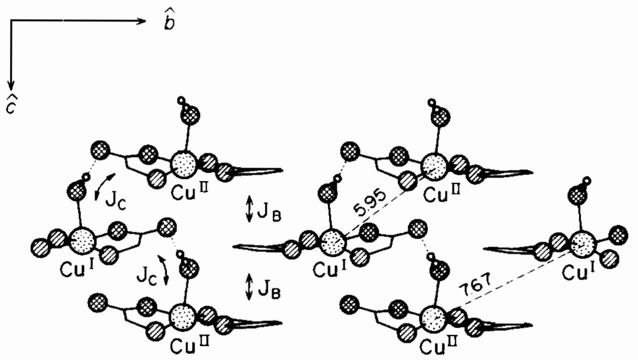

Fig. 4. Projection along the a axis of the Cu(asp)bpy crystal lattice [5] showing one of the layers of copper ions. The distances are given in Å. The side chain of the asp molecules are omitted for clarity.

using $\theta_c = 2S(S+1)zJ/3k_B$, as given by the molecular field theory [11], where $S = 1/2$, and $z = 4$ is the number of copper ions coupled to each copper ion.

Magnetic susceptibility measurements in the 116–300 K temperature range were also reported for Cu(asp)bpy by Antolini et al. [5], who obtained an antiferromagnetic behavior with $\theta_c = -25(1)$ K. We do not have an explanation for this large value.

3.3. EPR data

Considering the crystal structure of Cu(asp)bpy, four resonance lines corresponding to the four copper sites in the unit cell should be observed for an arbitrary magnetic field orientation. The planes of the ligands to the copper ions at sites I and IV, as well as those at sites II and III, are approximately parallel (see Fig. 3(b)). Then, these pairs of copper ions should give rise to the same EPR spectra, if we assume axially symmetric molecular g tensors. This fact and the conditions imposed by the symmetry operations relating copper ions in Cu(asp)bpy determine that the four copper sites give the same spectrum with B applied in the $xy = ab$ plane and along the axes a, b or c [12]. Then, two resonance lines should be observed in the zx and zy planes and one in the $xy = ab$ plane. The single resonance line observed in the zx and zy planes is due to the collapse by exchange interaction of the resonances corresponding to the two magnetically non-equivalent copper ions. This collapse cannot be produced by exchange interactions coupling non-equivalent copper spins in different layers (I with III, and II with IV), because these are very weak. Therefore, the superexchange interactions able to collapse the resonances are transmitted through chemical paths connecting copper ions within each layer (I with II, and III with IV) (see Fig. 4). Then, in order to analyze the EPR data, Cu(asp)bpy can be treated as a layered system with two magnetic non-equivalent rotated copper spins in each layer, which are coupled to give a single EPR signal. The two symmetry related layers in Cu(asp)bpy cannot be distinguished with EPR due to the above mentioned similar orientation of the normals to the ligand planes (see Fig. 3).

The largest magnetic interaction terms contributing to the energy of the system are

$$\mathscr{H} = \mathscr{H}^{\circ}_{z} + \mathscr{H}_{ex} + \mathscr{H}'_{z} + \mathscr{H}_{dd} + \mathscr{H}_{hfs} \tag{1}$$

with

$$\mathscr{H}^{\circ}_{z} = \beta S g B \tag{2}$$

where β is the Bohr magneton, S and g are the effective spin ($S = 1/2$) and the crystal g tensor of the copper ions, respectively, and B is the applied magnetic field. $\mathscr{H}^{\circ}_{z} + \mathscr{H}'_{z}$ is the Zeeman interaction: $\mathscr{H}^{\circ}_{z}$ considers the diagonal contribution while $\mathscr{H}'_{z}$ considers the non-diagonal part, different for the four sites in the unit cell in the orthorhombic axes system [1]. $\mathscr{H}_{ex}$ is the exchange interaction between copper spin pairs, which is assumed to be of Heisenberg type, $\mathscr{H}_{dd}$ is the magnetic dipolar interaction between copper ions, and $\mathscr{H}_{hfs}$ is the hyperfine interaction with the copper nucleus.

The position of the exchange collapsed resonance of the copper spins is described by $\mathscr{H}^{\circ}_{z}$ in Eq. (2). The crystal g tensor defined in Eq. (2) is the average of the molecular g tensors of the four copper sites in the unit cell. We evaluate the components of g^2 using the data in Fig. 1, and a least-squares procedure with the function $g^2(\theta,\phi) = hggh$, where $h = B/|B| = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, is the magnetic field orientation, and $g^2(\theta,\phi)$ is the observed variation of the squared g factor. The results obtained are shown in Table 1, and are used to obtain the solid lines in Fig. 1. Table 1 and Fig. 1 show that g^2 is approximately diagonal and axially symmetric. Considering the square planar configuration around the copper ions we assume axial symmetry for the molecular g tensors, with $g_\perp$ in the plane of the ligands and $g_\parallel$ along its normal. Considering that the b axis of the crystal is approximately contained in the plane of the ligands, we obtain $g_\perp = 2.06(1)$ from the value of $g^2(\theta,\phi)$ along this axis. Since the trace of g^2 is invariant under rotations of the reference system, we calculated $g_\parallel = 2.24(1)$. This is coincident with the value obtained by Antolini et al. in polycrystalline samples of Cu(asp)bpy [5]. The values of $g_\perp$ and $g_\parallel$ are in agreement with the overall axial symmetry observed in Cu(asp)bpy and indicate that the ground state orbital for the copper ions is $d(x^2-y^2)$ [13]. The value of $g_\parallel$ in Cu(asp)bpy is lower than that obtained for the polymeric compounds Cu(glu) ($g_\parallel = 2.345$) [1] and Cu(asp) ($g_\parallel = 2.312$) [2]. The symmetry around Cu(II) ions in the three compounds is similar, but the coordinations in Cu(glu) and Cu(asp) involve as equatorial ligands a water oxygen atom and an oxygen atom of the carboxylate group of the amino acid side chain. The replacement of these ligands by the nitrogen atoms of bpy produces the decrease of $g_\parallel$ in Cu(asp)bpy [2].

Table 1

$(g^2)_{ij}$ components[a] of the squared gyromagnetic tensor of Cu(asp)bpy obtained at 9.85 GHz and a_i parameter values

g^2 components [a]	a_i parameters [b]
$(g^2)_{xx} = 4.265(3)$	$a_1 = 30(2)$ G
$(g^2)_{yy} = 4.301(3)$	$a_2 = 17.6(8)$ G
$(g^2)_{zz} = 4.953(3)$	$a_3 = 4.5(4) \times 10^{-3}$ G^{-1}
$(g^2)_{xy} = -0.036(3)$	$a_4 = 219(17)$ G
$(g^2)_{xz} = (g^2)_{yz} = 0.000(3)$	$a_5 = 92(10)$ G

[a] Calculated by a least-squares fit of the function $g^2(\theta,\phi) = hggh$ to the data in Fig. 1, where $h = B/|B|$ is the direction of the applied field.

[b] Obtained by a least-squares fit of Eq. (4) to the linewidth data in Fig. 4.

The angular dependence of the EPR linewidth $\Delta B_{pp}(\theta,\phi)$ is a consequence of the last three terms of Eq. (1) modulated by the exchange interaction [14,15]. The second order angular contribution in the zx and zy planes arises mainly from the incomplete collapse of the hyperfine structure by the exchange interaction. The hyperfine interaction introduces a contribution to the linewidth proportional to the second moment of the secular part of the hyperfine Hamiltonian. Assuming that the principal directions of the molecular tensors g_i^2 and A_i^2 (i=I–IV) are coincident, the correlation observed between g^2 (Fig. 1) and $\Delta B_{pp}(\theta,\phi)$ (Fig. 2) in the zx and zy planes supports this broadening mechanism.

The fourth order angular variation of the linewidth in the $xy=ab$ plane is attributed to the dipolar interaction. The layered structure of the copper ions in Cu(asp)bpy (see Fig. 4), produces a spin dynamics having the long time behavior characteristic of the diffusive regimen in two-dimensional systems [16]. As shown in Fig. 2, the angular variation of the linewidth in the $xy=ab$ plane follows

$$\Delta B_{pp}(\theta,\phi) \propto (3\cos^2\theta_n - 1)^2 \tag{3}$$

as expected for a two-dimensional system, where θ_n is the angle between the direction of the magnetic field and the a axis normal to layers [16]. A fourth order angular variation may also be attributed to the Zeeman residual interaction $\mathscr{H}'_Z$. However, in this plane the four copper ions are magnetically equivalent and this contribution cancels out.

In order to perform a quantitative analysis, the experimental values of $\Delta B_{pp}(\theta,\phi)$ were least-squares fitted to a function which considers the broadening contributions discussed above.

$$\Delta B_{pp}(\theta,\phi) = a_1 + a_2(3\cos^2\theta_n - 1)^2 + a_3\frac{A^2(\theta,\phi)}{g^2\beta^2} + a_4(\sin\theta\cos\theta\sin\phi)^2 + a_5\cos^4\theta \tag{4}$$

The values of the a_i coefficients are given in Table 1, and are used to obtain the solid lines in Fig. 2. The a_1 term in Eq. (4) is an isotropic contribution to the linewidth, and a_2 takes into account the contribution of Eq. (3). The a_3 term in Eq. (4) is proportional to the second moment of the hyperfine interaction, where $A^2(\theta,\phi) = hAAh$ is the mean hyperfine tensor with the copper nucleus [17]. As in Ref. [17], in order to evaluate $A^2(\theta,\phi)$ we assume axially symmetric hyperfine tensors A_i^2, with eigenvalues $A_\parallel/g\beta = 180$ G, $A_\perp/g\beta = 20$ G, and the eigenvectors corresponding to $A_\parallel/g\beta$ along the direction of the normal to the plane of ligands of each copper ion. These values were used to evaluate the molecular tensors $A_i^2(\theta,\phi)$ in the crystalline axes a, b and c, and then averaged over the four copper sites i=I,...IV in order to obtain $A^2(\theta,\phi)$. The first three terms in Eq. (4) are the most important contributions to $\Delta B_{pp}(\theta,\phi)$, while the a_4 and a_5 terms improve the quality of the fit in the zx and zy planes, and may be interpreted as small contributions arising from the Zeeman residual interaction $\mathscr{H}'_Z$.

From the EPR data we can estimate the magnitude of the mean value of $|J|$. The collapse of the hyperfine structure of the copper ions along the c axis, and the collapse of the resonance lines of the two non-equivalent copper ions in the crystal lattice for any magnetic field orientation, put a lower limit $|J/k_B| \geqslant 0.02$ K to the isotropic exchange parameter between the copper ions. From the value of the coefficient a_3 we obtained $|J/k_B| = 0.20(3)$ K for the exchange interaction of one copper ion with its four nearest neighbors within a copper layer. In this calculation we used the 'abacus method' [18] with the corrections included in Ref. [17], which takes into account the broadening of the resonance due to the incomplete collapse of the hyperfine structure.

3.4. Exchange interaction and superexchange paths

Magnetically non-equivalent copper ions within one layer are connected by two types of superexchange paths. We call J_C the exchange parameter associated with the chemical path that involves a carboxylate bridge and a hydrogen bond, and J_B that associated with the stacking of the bipyridyl ligands (Fig. 4). The two-dimensional magnetic behavior shown by the EPR linewidth data, indicates that J_C and J_B have similar magnitudes. In fact, if $J_C \gg J_B$ or $J_C \ll J_B$, a one-dimensional behavior and therefore a different angular variation of the linewidth should be expected in the $xy=ab$ plane. The exchange parameter J_B mediated by the stacking involves the interaction between two approximately parallel bpy ligands separated by ≈3.6 Å. The π type MOs involved in this bond are inadequate to overlap with the lobes of the metal magnetic orbitals, which are directed toward the σ nitrogen orbitals [19], and suggests a positive sign for J_B. The analysis of J_C is complex because this path involves different types of bonds. To the σ bonds of the carboxylate bridges, and the electrostatic interaction of the hydrogen bonds, we should add the weakly covalent bond between a copper ion and the apical oxygen water ligand at 2.368 Å (see Fig. 4). To our knowledge, this type of superexchange path has not yet been studied and no conclusions can be inferred about the sign of J_C and its efficiency as a superexchange path. Further experimental and theoretical studies are necessary in order to have a better understanding of this problem. An alternative chemical path for J_C is the carboxylate bridge connecting the copper ions from an equatorial position to an apical position (see Fig. 4). It was not considered here taking into account the results of Levstein and Calvo [20].

They correlated the magnitude of $|J|$ through carboxylate bridges bridging copper ions in a way similar to the case of Cu(asp)bpy, as a function of the length of the copper–apical oxygen bond. This correlation predicts for the length of the Cu–O2 bond of Cu(asp)bpy (3.019 Å), a negligible value of the $|J|$ parameter.

4. Conclusions

The analysis of the EPR data in Cu(asp)bpy provides two types of information. The observed crystal g tensor interpreted in terms of axial molecular g tensors indicates a d(x^2–y^2) ground orbital state. The linewidth data are discussed in terms of the exchange interactions between copper ions. The angular dependence $\Delta B_{pp}(\theta,\phi)$ shows a contribution characteristic of a two-dimensional magnetic behavior. This indicates that the chemical paths connecting the copper ions within each layer contribute to the exchange network with similar magnitudes of J. There is a reasonable agreement for the exchange parameters obtained from EPR ($|J_C/k_B| \approx |J_B/k_B| =$ 0.20(3) K) and susceptibility measurements ($J/k_B=$ 0.12(4) K). The value of J_B indicates that the stacking of bipyridyl ligands contributes with a weak but not negligible superexchange interaction. Then, these hydrophobic interactions not only contribute to the stabilization of the crystal lattice, but they also provide superexchange paths for magnetic interactions between copper ions.

Structural data and susceptibility measurements in the 2–300 K temperature range indicate that Cu(asp)bpy is a molecular instead of a polymeric compound. On the other hand, EPR reveals a two-dimensional magnetic behavior. In this sense, this work corroborates the usefulness of the EPR experimental data for the magnetic characterization of weakly coupled compounds.

Acknowledgements

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