Antiferromagnetic Spin Chain Behavior and a Transition to 3D Magnetic Order in Cu(D,L-alanine)$_2$: Roles of H-bonds

Rafael Calvo$^a$, Rosana P. Sartoris$^a$, Hernán L. Calvo$^b$, Edson F. Chagas$^{c,d}$, Raúl E. Rapp$^c$

$^a$Departamento de Física, Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral, and Instituto de Física del Litoral (UNL–CONICET), Güemes 3450, 3000 Santa Fe, Argentina
$^b$Instituto de Física Enrique Gaviola (IFEG–CONICET) and FaMAF Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina
$^c$Instituto de Física, Universidade Federal do Rio de Janeiro, CP 68528, 21941-972, Rio de Janeiro RJ, Brazil
$^d$Instituto de Física, Universidade Federal de Mato Grosso, 78060-900, Cuiabá-MT, Brazil

Abstract

We study the spin chain behavior, a transition to 3D magnetic order and the magnitudes of the exchange interactions for the metal-amino acid complex Cu(D,L-alanine)$_2$H$_2$O, a model compound to investigate exchange couplings supported by chemical paths characteristic of biomolecules. Thermal and magnetic data were obtained as a function of temperature ($T$) and magnetic field ($B_0$). The magnetic contribution to the specific heat, measured between 0.48 and 30 K, displays above 1.8 K a 1D spin-chain behavior that can be fitted with an intrachain antiferromagnetic (AFM) exchange coupling constant $2J_0 = (−2.12 ± 0.08)$ cm$^{-1}$ (defined as $\mathcal{H}_{ex}(i,i+1) = −2J_0S_i · S_{i+1}$), between neighbor coppers at 4.49 Å along chains connected by non-covalent and H-bonds. We also observe a narrow specific heat peak at 0.89 K indicating a phase transition to a 3D magnetically ordered phase. Magnetization curves at fixed $T = 2$, 4 and 7 K with $B_0$ between 0 and 9 T, and at $T$ between 2 and 300 K with several fixed values of $B_0$ were globally fitted by an intrachain AFM exchange coupling constant $2J_B = (−0.27 ± 0.02)$ cm$^{-1}$ and $g = 2.091 ± 0.005$. Interchain interactions $J_1$ between coppers in neighbor chains connected through long chemical paths with total length of 9.51 Å cannot be estimated from magnetization curves. However, observation of the phase transition in the specific heat data allows estimating the range $0.1 \leq |2J_1| \leq 0.4$ cm$^{-1}$, covering the predictions of various approximations. We analyze the magnitudes of $2J_0$ and $2J_1$ in terms of the structure of the corresponding chemical paths. The main contribution in supporting the intrachain interaction is assigned to H-bonds while the interchain interactions are supported by paths containing H-bonds and carboxylate bridges, with the role of the H-bonds being predominant. We compare the obtained intrachain coupling with studies of compounds showing similar behavior and discuss the validity of the approximations allowing to calculate the interchain interactions.

Keywords: Spin chains; Phase transition; Exchange interactions; H-bonds

1. Introduction

One-dimensional (1D) spin-chains provide insights on treating soluble quantum many-body problems, and became paradigmatic since the origins of quantum mechanics [1][4]. The interest flourished when it was observed that chain compounds of metal ions with inorganic and organic ligands really exist in nature [5][7], and that their thermodynamic properties can be modeled by the theories [8][12]. The compound copper tetramine sulfate monohydrate, CTS = Cu(NH$_3$)$_4$SO$_4$·H$_2$O, was found to have 1D antiferromagnetic (AFM) behavior above 0.5 K [5][6], that was attributed to Cu$^{II}$ ions located in chains parallel to the $a$-axis [13] linked as Cu$^{II}$—H$_2$O—Cu$^{II}$—H$_2$O—Cu$^{II}$, a result that started important theoretical developments that have also been helpful to deal with other problems [2] such as molecular magnets [3][12][14], superconductivity [15], quantum dissipation [16], and quantum communication [17].

Mermin and Wagner [18] proved that at any nonzero temperature ($T$), 1D or 2D isotropic spin Heisenberg model with finite-range exchange interaction can be neither FM nor AFM, and no transitions to ordered phases should occur by lowering $T$. However, in any real system, small interactions between chains (or layers) exist, introducing new ingredients to the problem. One indication of these interactions are phase transitions to long
range magnetically ordered phases which have been observed in “quasi” 1D spin chains involving inorganic and organic ligands. For example, a transition arising from exchange couplings between CuIII in neighbor chains was observed [6] in the specific heat of CTS at $T = 0.37 \text{ K}$ and attributed to interactions through weak \cdots \cdot CuIII\text{--}NH_3\text{--}SO_3\text{--}NH_3\text{--}CuIII \cdots paths containing H-bonds. Further EPR experiments [19, 21] introduced doubts in the interpretation of the data about CTS, the compound that promoted the first theoretical advances about the thermodynamic properties of spin chains [8, 9]. In any case, this and other low-dimensional compounds provided a full source of information about thermodynamic properties and spin dynamics. The relationship between weak interchain interactions and phase transitions was studied experimentally [6, 7, 22], and theoretically [4, 23–32], to evaluate these weak interactions and to verify the applicability of the subjacent theories.

The crystal and electronic structures of metal-amino acid and metal-peptide compounds provide model systems for metalloproteins in their active sites [33]. The amino acid side chains of these weak interactions and to verify the applicability of the subjacent theories. The crystal and electronic structures of metal-amino acid and metal-peptide compounds provide model systems for metalloproteins in their active sites [33].

**2. Experimental procedures**

Basic copper carbonate (0.5 mmol) was added to a solution of the racem mixture D,L-alanine (2 mmol in 20 mL of hot water). After kept at 60°C until the reaction was complete, the remaining insoluble copper carbonate was filtered out with Millipore membranes having pore size 0.22 μm. Single crystals of good quality with sizes up to $4 \times 2 \times 2 \text{ mm}^3$ were obtained in about two weeks by slow evaporation of the solution at 40°C. The compound is stable, allowing accurate magnetic measurements.

The heat capacity was measured in the $T$ range 0.48 < $T < 30 \text{ K}$ with a semi-adiabatic calorimeter mounted in a pumped $^3\text{He}$ cryostat. The polycrystalline sample was prepared as to improve the low thermal conductivity of the organic material at low $T$ [48, 49, 62]. About 100 mg of powdered crystals of Cu(D,L-alanine)$_2$ with particle size of about 100 μm were mixed to about the same mass of powdered copper with particle size of about 5 μm, to obtain a good thermal conducting copper path around each sample particle, while keeping small
the contribution of the metallic copper. The sample-copper mixture was compressed inside a cylindrical holder made of 0.04 mm thick copper foil, forming a chip, and allowing obtaining a temperature equilibration time constant < 25 seconds within the sample, in the full measuring range. This chip was glued with vacuum grease to a copper plate fixed to the calorimeter, where the thermometer and heater were attached. This method allows fast replacement of samples in the calorimeter, and avoids destroying them after the measurement. Heat was applied during intervals of about 100 seconds as to produce T changes of 1%. The calorimeter addendum heat capacity, always smaller than 1% of that of the sample, was measured independently. The heat capacity of the sample, C_{exp}, was obtained subtracting the contribution of the copper (powder and foil) from the total heat capacity of the chip. The dispersion of the data was less than 2%.

A commercial PPMS magnetometer (Quantum Design, Inc., San Diego, CA) was used to measure the magnetization using a powder sample of (56.4 ± 0.3) mg of Cu(D,L-ala)_2. The contribution of the sample holder was measured separately, and subtracted from the results. Isothermal magnetization curves at T = 2, 4 and 7 K with B_0 up to 9 T, and magnetization curves with T between 2 and 90 K, for several applied fields B_0, were obtained. All reported magnetic measurements were corrected for diamagnetism using standard values estimated from Pascal constants and TIP [11,12]. The susceptibility χ_0(T) calculated from magnetization data obtained with B_0 = 0.1 T reproduce previous results [41].

3. Crystal structure of Cu(D,L-ala)_2 monohydrate

The structure is monoclinic, space group C2/c (# 15) with a = 12.087 Å, b = 9.583 Å, c = 8.973 Å, β = 110.85°, and Z = 4 molecules [Cu(NH_2CHCH_3CO_2)_2H_2O] in the unit cell [41,60]. Two of these molecules (called A and B) are related by a rotation of 180° around the b-axis. The other two are related to the first ones by a translation within the unit cell. The copper ions are in an elongated centrosymmetric nearly octahedral coordination, equatorially bonded to two amino nitrogens and two carboxylate oxygens of D and L amino acid molecules, and apically bonded to two oxygens O_w from water molecules. Alternate rotated copper ions types A and B at 4.487 Å are arranged in chains along the c-axis (see Fig. [1]), sharing the O_w ligands providing an intrachain exchange path Cu_A—O_w—Cu_B with total bond length 5.368 Å and angle of 113.4°. Contribute to this bridge two “moderate” [63,64] symmetry-related H-bonds Cu_A—N_eq—H···O_eq—Cu_B with d(N—O) = 3.015 Å, typical of amino acid and protein structures [43], and total path-length 6.982 Å, connecting equatorial N and O ligands to coppers, similar to superexchange paths studied before in other copper amino acid compounds [48,49,51]. In comparison, Muhonen [65] and Talukder et al. [66] reported the structures and magnetic properties of the dinuclear compounds [Cu_2(C_2H_10NO_2)(C_4H_11NO_2)(H_2O)][ClC_7H_5O_2]_2·2C_3H_7OH and [Cu_2(μ_2-H_2O)L_2(H_2O)_2][ClO_4]_2·2H_2O having pairs of copper ions bridged by water molecules and two symmetry related H-bonds as neighbor copper ions in the chains of Cu(D,L-ala)_2 (see later). Uekusa et al. [67] reported other dinuclear CuII compound bridged by a water molecule; however, in this case also contribute two equatorial carboxylate bridges that introduce deep differences in the magnetic behavior.

In Cu(D,L-ala)_2 all chains are related by translations (so, EPR measurements do not provide information about interchain interactions) [59] and each one is surrounded by other four, at equal distances 7.712 Å (Fig. 2). A copper ion type A (in the center of the unit cell in Fig. 2) has four type A copper nearest neighbors at 7.712 Å, and eight copper ions type B in the vertices of the monoclinic unit cell, in neighbor chains. Four AB pairs are at 7.766 Å, and the other four at 9.945 Å; we consider only the interactions between coppers at the shorter distance, connected by a chemical path Cu_A—O_eq—C···O···H···N_eq—Cu_B, with five diamagnetic atoms and total path length of 9.508 Å, including a H-bond with length 3.062 Å and a carboxylate bridge.
Cu(D,L-alanine)$_2$ distinguishes different regimes. For $T > 7$ K, \( \log(C_{\text{exp}}(T)/R) \) increases linearly with \( \log(T) \) and we extrapolate \( C_{\text{int}}(T)/R = 234(T/\Theta_0)^3 = 2.58 \times 10^{-3}T^3 \), as predicted for the lattice vibrational contribution \[69\] with a Debye temperature \( \Theta_0 \approx 97 \) K, and assuming that at high \( T \) the asymptotic behavior of the magnetic contribution is \( C_{\text{mag}} \propto T^{-2} \) \[11\]. For $T < 7$ K \( C_{\text{int}} \) is small, and Fig. 3 shows that the \( C_{\text{mag}}(T)/R = (C_{\text{exp}} - C_{\text{int}})/R \) vs. \( T \) curve displays a broad peak at \( T_{\text{max}} = 1.8 \) K, and a narrow peak at \( T_N = 0.89 \) K. Below \( 0.89 \) K, see Figs. 3b and b, the magnetic contribution to the specific heat follows \( C_{\text{mag}}/R \approx 1.18T^2 \) down to 0.55 K where small deviations start to occur. The nature of the peaks in \( C_{\text{mag}}(T) \) (see Fig. 3b) is understood by calculating the magnetic entropy \( S_{\text{mag}}(T) \) for \( T \rightarrow \infty \). We estimate first \( S_{\text{mag}}(0.48 \text{ K}) = 0.0576R \), and then we integrate numerically the experimental result in Fig. 3b such that:

\[
S_{\text{mag}}(T \rightarrow \infty) = S_{\text{mag}}(0.48 \text{ K}) + \int_{0.48 \text{ K}}^{T} C_{\text{mag}}(T)/R dT,
\]

where \( C_{\text{mag}}(T) = 0 \) for \( T \geq 12 \) K, and \( S_{\text{mag}}(\infty)/R = 0.683 \) approaches asymptotically the value \( \ln(2) = 0.693 \) expected for the spin 1/2 system. Thus, considering the structural information \[41\] \[50\], the data in Fig. 3b indicates that the broad peak of \( C_{\text{mag}} \) at 1.8 K arises from short range ordering within spin chains antiferromagnetically coupled by \( 2J_0 \) and the narrow peak at \( T_N = 0.89 \) K marks the transition to a 3D magneti-
cally ordered phase, where spin correlation between the chains is reached. This transition would be related to the exchange couplings $2J_1$ between Cu$^{II}$ ions in neighbor chains.

Figure 4 displays molecular magnetization $M/N_{Av}$ isotherms of the powder sample of Cu(DL-alad)$_2$ at $T = 2$, 4, and 7 K, between 0 and 9 T that show saturation effects at high fields. Fig. 4 displays $M/N_{Av}$ for various fixed values of $B_0$ and 2 $\leq T$ $\leq$ 85 K.

5. Theory and analysis

We describe first the thermal and magnetic properties of isolated spin chains using the method of Bonner and Fisher [8] (BF) and calculate the intra-chain exchange couplings. Later, we estimate the exchange couplings between Cu$^{II}$ ions in neighbor chains, considering the observed magnetic phase transition at 0.89 K and following different approximate theories (mean field, spin waves and others).

5.1. Spin-chains thermodynamics

A uniform spin-chain with $N_S$ spins having isotropic exchange coupling $2J_0$ between nearest neighbor spins and isotropic g-factor, under a static field $B_0$, is described by the sum of exchange and Zeeman interactions [9].

$$H_{ch}^{N_S} = |J_0| \sum_{i=1}^{N_S} \left[ \frac{2J_0}{|J_0|} S_i \cdot S_{i+1} + y S_i^z \right] = |J_0| H_{ch}^{N_S},$$

where $y = g \mu_B B_0/|J_0|$ is the reduced magnetic field and $S_i^z$ is the z-component of the i-copper spin in the chain, and we use periodic conditions (i.e., spin rings with $S_{N_S+1} = S_1$) [8][22]. In powder samples, the g-factor is the angular average of the g-matrix of the Cu$^{II}$ ions. The molar specific heat $C_{mag}$, and molecular magnetization $M/N_{Av}$ for finite chains of $N_S$ spins may be calculated as a function of $T$ and $B_0$ with the BF’s method [8] using Eq. 2 and the eigenstates of the chains through [8][22][70]:

$$C_{mag}(T) = \frac{R}{N_S x^2} \left[ (\langle H_{ch}^{N_S} \rangle)^2 - \langle H_{ch}^{N_S} \rangle^2 \right],$$

$$M(B_0, T) = \frac{g \mu_B}{N_S} \langle S_z \rangle,$$

where $x = k_B T/|J_0|$ is the “reduced temperature.” The angle brackets in Eqs. 3 and 4 are thermal averages of the enclosed operators for chains with $N_S$ spins, at $T$ and $B_0$ (for $C_{mag} , B_0 = 0$) [22][35]:

$$\langle H_{ch}^{N_S} \rangle = \frac{1}{Z} \sum_{k=1}^{M} E_k \exp (-J_0 E_k/k_B T),$$

$$\langle S_z \rangle = \frac{1}{Z} \sum_{k=1}^{M} s^z_k \exp (-J_0 E_k/k_B T),$$

where $Z = \sum_{k=1}^{M} \exp (-J_0 E_k/k_B T)$, and $k$ labels the $M = 2^{N_S}$ states of the chain having a spin $z$-component $s^z_k$. The energy $E_k$ of the $k$-state of the Hamiltonian $H_{ch}^{N_S}$ is:

$$E_k = \epsilon_{k,0} + y s^z_k,$$

where $\epsilon_{k,0}$ are the energies of the states in the absence of $B_0$ and in units of $|J_0|$. The thermodynamic variables for infinite chains are obtained by extrapolating to $N_S \rightarrow \infty$ the results for finite chains [8]. We confirmed that within the considered $T$-range, chains of 20 spins provide results as valid as infinite chains and used Eq. 2 with their eigenvalues [22] to fit our specific heat data above 1.8 K (Fig. 3b), obtaining $2J_0 = (-2.12 \pm 0.08)$ cm$^{-1}$ and the red solid line in this figure. Also, Eq. 4 was fitted to the whole set of magnetization data in Fig. 4 by obtaining:

$$g = 2.091 \pm 0.005 and 2J_0 = (-2.27 \pm 0.02) \text{ cm}^{-1}.$$
C\text{mag}(T)$ below the transition temperature $T_N$ should behave as $7^{[24]} 26$:

$$C_{\text{mag}(sw)} \propto T^{d/n}, \quad (8)$$

where $d = 3$ is the magnetic dimension at low $T$ and $n = 1$ for AFM and $n = 2$ for FM couplings. So, the experimental result $C_{\text{mag}}/R \propto T^3$ below $T_N$ reflects an AFM 3D ordering below 0.89 K. Small deviations at the lowest $T$ are justified because, besides $2J_1$, other non-negligible interchain interactions may contribute (see Figs. 1 and 2), and because of the low lattice space symmetry. We first estimated $2J_1$ using the sw results of Sorai et al. $24^{[24]} 26$, considering axial symmetry around the chain axis, with exchange coupling $2J_0$ along the spin chains, and $2J_1$ between chains, using $24^{[24]}$:

$$C_{\text{mag}(sw)}/R = \frac{\zeta(4)\Gamma(4)k_B^2}{16\pi^2S^3V} T^3, \quad (9)$$

and comparing with the experimental result, $C_{\text{mag}}/R \approx 1.18T^3$. $\zeta(4) = \pi^4/90$ is Riemann’s zeta function and $\Gamma(4) = 3!$ is Euler’s gamma function, and $24^{[24]}$.

$$V = \begin{cases} \frac{(|J_0| + 2|J_1|)^3}{J_0^2 J_1^3} & \text{for } J_1 < 0 \\ \frac{|J_0^2 J_1|}{|J_0|} & \text{for } J_1 > 0. \end{cases} \quad (10)$$

So, for $2J_0 = -2.27\text{ cm}^{-1}$ and $J_1 < 0$, it is $2J_1 = -0.125\text{ cm}^{-1}$, while for $J_1 > 0$, it is $2J_1 = 0.146\text{ cm}^{-1}$. Meanwhile, assuming axial symmetry around the chain axis and defining $\eta = |J_1/J_0|$, the mean field (mf) theory of Oguchi gives: $27$

$$k_B T_N/|J_0| = \frac{4S(S + 1)}{3} \frac{I(\eta)}{I(\eta)} \quad (11)$$

where $27^{[27]} 71^{[71]} 72^{[72]}$.

$$I(\eta) \approx 0.64\eta^{-1/2} \quad (12)$$

Equations $11$ and $12$ allow estimating the ratio $\eta = 0.122$ from the experimental values of $T_N$ and $2J_0$ and so $|2J_1| = 0.28\text{ cm}^{-1}$. In addition to these sw and mf estimates for the interchain coupling, we now turn to more recent analyses for the transition temperature in low-dimensional systems based on a mean-field theory within a random-phase approximation (RPA) $25^{[25]} 30^{[30]}$. According Schulz $29^{[29]}$, the mean-field treatment of the full 3D Hamiltonian yields for the interchain coupling within RPA:

$$\eta = \frac{k_B T_N/|2J_0|}{4c \ln^{1/2} \frac{4|2J_0|}{k_B T_N}}, \quad (13)$$

where $c = 0.32$ and $\lambda = 5.8$ were estimated from numerical calculations in a single chain $73^{[73]}$. Therefore, $\eta = 0.122$ and hence we obtain the same $2J_1$ as Oguchi’s estimate. The agreement between the two estimates is, however, accidental, since these approximations predict different scalings for the transition temperature. A modified RPA approach was reported by Irkhin and Katanin $30^{[30]}$ in which the exchange ratio obeys:

$$\eta = \frac{k_B T_N/|2J_0|}{4c \sqrt{\ln \frac{4|2J_0|}{k_B T_N}} + \frac{1}{2} \ln \frac{4|2J_0|}{k_B T_N}}, \quad (14)$$

where $c = 0.23$ includes a correction factor $\sim 0.7$ accounting for spin fluctuation along the directions perpendicular to the chains. $30^{[30]}$ In this case we obtain $|2J_1| = 0.36\text{ cm}^{-1}$.

The same expression as Eq. $14$ is given “empirically” by Yasuda et al. $31^{[31]}$, where a numerical fit based in quantum Monte Carlo (QMC) simulations yields $c = 0.233$ and $\lambda = 2.6$ and the interchain interaction in Cu(0,L-ala)$_2$ results $|2J_1| = 0.41\text{ cm}^{-1}$.
6. Discussion

In this work we studied the specific heat and magnetization for the copper amino acid salt \( \text{Cu(D,L-ala)}_2 \) in a wide temperature and magnetic field range. The compound displays a clear 1D spin chain behavior above \( \sim 1.8 \) K, that was observed in a previous work based in basic susceptibility data \([41]\). Our present data allows a precise characterization of this spin chain behavior and adds up to detect a 3D magnetic phase transition at 0.89 K that was analyzed under different approximations in order to evaluate the exchange interactions \( 2J \). We also analyze the values of \( \eta \) that was analyzed under different approximations in order to evaluate the exchange interactions \( 2J \) between coppers in neighbor chains. Here we compare the results of these estimations. We also analyze the values of \( 2J_0 \) and \( 2J_1 \) in terms of the chemical paths connecting the copper ions and the roles of H-bonds in supporting exchange couplings.

6.1. Discussion of the magnitudes of the interchain interactions

Since no direct evaluation of the interchain coupling is available for \( \text{Cu(D,L-ala)}_2 \), the comparison between the estimated values of \( 2J \) is indeed subjected to the assumptions made in the considered approximations. On one hand, the mf estimations exhibit a systematic increasing of the ratio \( \eta = |J_1/J_0| \) in Oguchi \([27]\) and Schulz \([29]\) \( (\eta = 0.12) \) and Irkhin and Katanin \([50]\) \( (\eta = 0.16) \), as compared with the QMC result \([31]\) \( \eta = 0.18 \), that can be attributed to an overestimated critical temperature \( T_\lambda \), since in these approximations thermal and quantum fluctuations, which tend to inhibit the phase transition, are taken into account perturbatively. On the other hand, the spin-wave approach \([24, 26]\) estimates a smaller ratio \( \eta = 0.06 \), which may indicate failures in the collective-mode description near the critical temperature \( T_\lambda \).

The rather large value of the ratio \( \eta \), due to a transition temperature \( k_B T_\lambda = 0.27 |2J_0| \), suggests that the chains are not as well isolated as in other compounds (see, e.g. \( \text{Ref. [14]} \)). This was surprising considering the relatively long chemical path connecting neighbor chains as compared with those involved in the intrachain exchange coupling. An explanation is that the intervening carboxylate bridge in the interchain chemical path would act as a “short circuit”, leaving the H-bond in series as the dominant contribution to \( 2J_1 \).

It is important to notice that the above estimates are based on models where the underlying lattice structure is highly symmetric, while in \( \text{Cu(D,L-ala)}_2 \) these symmetries are clearly absent. In particular, the studied effective coupling between neighbor chains in the compound’s monoclinic structure is not strictly perpendicular to the direction of the chains, as can be seen in Fig. 2 and thereby the above invoked axial symmetry is accomplished only partially. Besides, other interchain couplings like the aforementioned \( 2J \) may also introduce deviations with respect to the simplified approximations, where a single interchain exchange path is accounted for. With this unclear situation we opted to report a wide range \( 0.1 \leq |2J_1| \leq 0.4 \) cm\(^{-1} \) for the interchain interactions, and analyze this result below.

6.2. Magnetostructural correlations of intrachain and interchain interactions

As shown by Figs. 1 and 2, the structure \([41, 60]\) of \( \text{Cu(D,L-ala)}_2 \) clearly indicates that the observed 1D magnetic behavior arises from chains along \( c \), where pairs of neighbor coppers ions at 4.487 Å share a water apical oxygen atom. Also contribute to this exchange path two symmetry-related H-bonds with total path length 6.982 Å connecting N and O equatorial ligands to copper ions and N—O lengths 3.015 Å. This AFM superexchange interaction \( 2J_0 = -2.27 \text{ cm}^{-1} \), arises from a quantum process described by several authors \([12, 75–77]\), and cases where more than one bond contribute have been treated by Levstein et al. \([73]\), who discussed rules to tune these paths in order to maximize the coupling. We analyzed the relative role of the water oxygens and the H-bonds and propose that the water oxygen paths in \( \text{Cu(D,L-ala)}_2 \) (apical ligand to neighbor coppers along \( c \) do not play an important role in the coupling because the overlap between the involved magnetic orbitals is expected to be very small. We further support this assumption considering that these are “moderate” H-bonds \([63, 64]\) and their individual contributions add up due to symmetry conditions \([78]\). Assuming that the main contribution to the interaction \( 2J_0 \) arises from the symmetry related H-bonds described before is in line with the arguments given by Muhonen \([65]\) and Talukder et al. \([66]\). The much larger exchange couplings reported in these cases may be attributed to much shorter and stronger H-bonds with total lengths \( d = 2.45 \) and 2.63 Å, respectively. The results of the DFT calculations of \( 2J_0 \) of Talukder et al. \([66]\), including and neglecting the water oxygen in the exchange path, also support our assumption. We also consider the results for the complexes of copper with the L-amino butyric acid (L-but) and with its racemic mixture (D,L-but) \([48, 51]\), where H-bonds with properties similar to those along \( c \) in \( \text{Cu(D,L-ala)}_2 \) support AFM exchange interactions \( 2J_0 = -1.28 \) and \( -1.68 \text{ cm}^{-1} \) in \( \text{Cu(L-but)}_2 \) and \( \text{Cu(D,L-but)}_2 \), respectively. In these cases the two H-bonds are slightly different in \( \text{Cu(L-but)}_2 \) but symmetry related in \( \text{Cu(D,L-but)}_2 \), with total
that the exchange lengths vary from 6.982 Å to 9.508 Å in the intrachain path, and the number of diamagnetic atoms in the paths vary from 3 to 5, respectively. Considering that the close values of \(J_\perp\) and \(J_0\) suggest that the covalent carboxylate bridge in 2\(J_1\) introduces a small effect in the overall magnitude of the interaction so the contribution from the H-bond would be the dominant one.

7. Conclusions

The specific heat and magnetization of the compound Cu(D,L-alanine)\(_2\) display above \(T = 1.8\) K, a well-defined 1D AFM behavior with \(J_0 = (-2.27 \pm 0.02)\) cm\(^{-1}\) and \(g = 2.091 \pm 0.005\). Considering the crystal structure the exchange interaction between neighbor coppers is undoubtedly supported by a chemical path containing an apical water oxygen ligand and two symmetry related H-bonds connecting equatorial oxygen and nitrogen ligands to copper. However, we attribute the main contribution to this interaction to the H-bonds, neglecting the effect of the water molecule. The specific heat data displays a transition to AFM 3D order at \(T_N = 0.89\) K. This result is used to estimate under different approximations a wide range of \(0.1 \leq |2J_1| \leq 0.4\) cm\(^{-1}\) for the exchange interaction coupling spins in neighbor chains that are supported by paths with total length of 9.5 Å. The relatively close magnitudes of inter- and intrachain couplings may suggest that the carboxylate bridge acts as a “short circuit” and has little influence in 2\(J_1\), leaving the H-bond as its principal contributor.

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References

[1] H. Bethe, On the theory of metals. I. Eigenvalues and eigenfunctions of a linear chain of atoms, Z. Phys. 71 (1931) 205–226. doi:10.1007/BF01341708
[2] D. C. Mattis, The Many Body Problem. An Encyclopedia of Exactly Solved Models in One Dimension, World Scientific Publishing Co. Pte. Ltd., Singapore, 1993.
[3] R. Georges, J. J. Borras-Almenar, E. Coronado, J. Curély, M. Drillon, One-Dimensional Magnetism: An Overview of the Models, in: J. S. Miller, M. Drillon (Eds.), Magnetism: Molecules to Materials I. Models and Experiments, Wiley-VCH, Weinheim, 2001, Ch. 1, pp. 1–47.
[4] T. Giamarchi, Quantum Physics in One Dimension, Oxford University Press, Oxford, 2003.
[5] J. J. Fritz, H. L. Pinch, Heat capacity and magnetic susceptibility of copper (II) tetrammine sulfate monohydrate from 1.3 to 24K, J. Am. Chem. Soc. 79 (1957) 3644–3646. doi:10.1021/ja01571a008
[6] T. Haseda, A. R. Miedema, Specific heat of Cu(NH\(_3\))\(_4\)SO\(_4\).H\(_2\)O below 1K, Physica 27 (1961) 1102–1112. doi:10.1016/0031-8914(61)90581-9
[7] L. J. de Jongh, A. R. Miedema, Experiments on simple magnetic model systems, Adv. Phys. 23 (1974) 1–224. doi:10.1080/0001873700101558
[8] J. C. Bonner, M. E. Fisher, Linear magnetic chains with anisotropic couplings, Phys. Rev. 135 (1964) A640–A658. doi:10.1103/PhysRev.135.A640
[9] R. B. Griffiths, Evidence for exchange coupled linear chains in Cu(NH\(_3\))\(_4\)SO\(_4\).H\(_2\)O, Phys. Rev. 135 (1964) A659–A660. doi:10.1103/PhysRev.135.A659
[10] R. B. Griffiths, Magnetization curve at zero temperature for the antiferromagnetic Heisenberg linear chain, Phys. Rev. 133 (1964) A768–A775. doi:10.1103/PhysRev.133.A768
[11] R. L. Carlin, Magnetocchemistry, Springer-Verlag, Berlin, 1986.
[12] O. Kahn, Molecular Magnetism, Wiley VCH, New York, 1993.
[13] B. Morosin, The crystal structures of copper tetrammine complexes. A. Cu(NH\(_3\))\(_4\)SO\(_2\).H\(_2\)O and Cu(NH\(_3\))\(_4\)SeO\(_4\), Acta Crystallogr. B 25 (1969) 19–30. doi:10.1107/S0567740869001725
[14] S. J. Blundell, Molecular magnets, Contemp. Phys. 48 (2007) 275–290. doi:10.1080/00107510701967415
[15] T. Vuletić, B. Korin-Hamzić, T. Ivec, S. Tomić, B. Goršunov, M. Dressel, J. Akimitsu, The spin-ladder and spin-chain system (La,Y,Sr,Ca)\(_{14}\)Cu\(_{24}\)O\(_{41}\): Electronic phases, charge and spin dynamics, Phys. Rep. 428 (2006) 169–258. doi:10.1016/j.physrep.2006.01.005
[16] F. Werner, M. Troyer, S. Sachdev, Quantum spin chains with site dissipation, J. Phys. Soc. Jpn. 74 (2005) 67–70. doi:10.1143/JPSJS.74S.67
[17] S. Bose, Quantum communication through spin chain dynamics: an introductory overview, Contemp. Phys. 48 (2007) 13–30. doi:10.1080/00107510701342313
[18] N. D. Mermin, H. Wagner, Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models, Phys. Rev. Lett. 17 (1966) 1133–1136. doi:10.1103/PhysRevLett.17.1133
[19] M. Date, M. Motokawa, H. Horii, S.-I. Kuroda, K.-I. Matsui, Is CTS a one-dimensional magnet?, J. Phys. Soc. Jpn. 39 (1979) 257–258. doi:10.1143/JPSJ.38.267
[20] W. Delfy, F. M. Weinhaus, D. L. Strandburg, Evidence for exchange-coupled quadratic nets in CTS, Phys. Lett. A 59 (1977) 491–493. doi:10.1016/0375-9601(77)90667-3
[21] H. Molyombo, E. Fujiwara, M. Motokawa, M. Date, High field magnetization of low-dimensional Heisenberg antiferro-
magnets, J. Phys. Soc. Jpn. 48 (1980) 1771–1772. doi:10.1143/JPSJ.48.1771

[22] E. F. Chagas, R. E. Rapp, D. E. Rodrigues, N. M. C. Casado, R. Calvo, Magnetic properties of ferromagnetic quasi-1D copper-peptide compounds: Exchange interactions and very low temperature phase transitions, J. Phys. Chem. B 110 (2006) 8052–8063. doi:10.1021/jp056838v

[23] T. Oguchi, A theory of antiferromagnetism, I. Prog. Theor. Phys. 13 (1955) 148–159. doi:10.1143/PTP.13.148

[24] N. Ohnma, A. Kajiwara, Y. Miyazaki, M. Kamachi, M. Sorai, Very low-temperature heat capacities and magnetic thermal anomalies of the organic free radical magnet, 4-methacryloylaminol-2,6,6-tetramethylpiperidine-1-oxyl (MATMP), Thermochim. Acta 267 (1995) 435–444. doi:10.10160/0040-6031(95)02501-4

[25] T. Matsunoto, Y. Miyazaki, A. S. Albrecht, C. P. Landee, C. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, A. J. Costa-Filho, O. R. Nascimento, L. Ghivelder, R. Calvo, C. D. Brondino, N. M. C. Casado, M. C. G. Passeggi, R. Calvo, T. Sakakibara, Y. Miyazaki, T. Ishida, T. Nogami, M. Sorai, J. S. Smart, E. Eff, R. Calvo, Magnetic properties of ferromagnetic quasi-LTMP, Thermochim. Acta 267 (1995) 435–444.

[26] J. Kokalj, J. Herbrych, A. Zheludev, P. Prelovsek, Antiferromagnets, J. Phys. Soc. Jpn. 48 (1980) 1771–1772. doi:10.1103/PhysRevB.13.4093

[27] R. Calvo, P. R. Levstein, E. E. Castellano, S. M. Fabiane, O. E. Piro, S. B. Oseroff, Crystal structure and magnetic interactions in Biss(D,L-Alaninato)Copper(II) hydrate, Inorg. Chem. 30 (1991) 216–220. doi:10.1021/ic00092a015

[28] R. Calvo, M. C. G. Passeggi, N. O. Moreno, G. E. Barberis, A. B. Chaves, B. C. M. Torres, L. Lezama, T. Rojo, Magnetic properties of Cu(L-aspartato)(H2O)2: A linear chain antiferromagnet, Phys. Rev. B 60 (1999) 1197–1203. doi:10.1103/PhysRevB.60.1197

[29] A. C. Rizzi, C. D. Brondino, R. Calvo, R. Baggio, M. T. Garland, R. E. Rapp, Structure and magnetic properties of layered high-spin Co(II)L-threoninate(H2O)2, Inorg. Chem. 42 (2003) 4409–4416. doi:10.1021/ic026111b

[30] M. F. Gerard, C. Aiassa, N. M. C. Casado, R. C. Santana, M. Perec, R. E. Rapp, R. Calvo, Magnetic properties and EPR spectra of [Cu(L-arginine)2(NO3)2(H2O)6], J. Phys. Chem. Solids 68 (2007) 1533–1539. doi:10.1016/j.jpcs.2007.03.032

[31] R. Calvo, M. C. G. Passeggi, M. A. Novak, O. G. Symko, B. Oeroff, O. R. Nascimento, M. C. Terrile, Exchange interactions and magnetic dimension in Cu(L-alamine)2: Specific heat measurements, J. Phys. Condens. Matter 7 (1995) 9595–9605. doi:10.1088/0953-8984/7/49/021

[32] R. Calvo, M. C. G. Passeggi, Shifts with temperature of the EPR spectra of [Cu(L-arginine)2](NO3)23H2O, J. Phys. Chem. 91 (1987) 133–140. doi:10.1021/j100333a028
signal in Cu(L-alanine)\textsubscript{2}: A low-dimensional paramagnet, Phys. Rev. B 44 (1991) 5111–5119. doi:10.1103/PhysRevB.44.5111

5111

[53] D. M. Martino, M. C. G. Passeggi, R. Calvo, Magnetic interactions in Cu(L-isoleucine)\textsubscript{2}H\textsubscript{2}O: An EPR experiment, Phys. Rev. B 52 (1995) 9466–9476. doi:10.1103/PhysRevB.52.9466

9466

[54] D. M. Martino, M. C. G. Passeggi, R. Calvo, O. R. Nascimento, EPR spectroscopy and exchange interaction parameters in Cu\textsubscript{2}(glycine)\textsubscript{2}H\textsubscript{2}O. Physica B 225 (1996) 63–75. doi:10.1016/0921-4526(96)00021-1

63

[55] A. J. Costa-Filho, O. R. Nascimento, R. Calvo, Electron paramagnetic resonance study of weak exchange interactions between metal ions in a model system: Cu\textsuperscript{2+}Gly-Trp. J. Phys. Chem. B 108 (2004) 9459–9455. doi:10.1021/jp047271r

9459

[56] S. P. Neuman, E. Winkler, O. Peña, M. C. G. Passeggi, A. C. G. Szalontai, R. Csonka, G. Speier, J. Kaizer, J. Sabolovič, T. Sandreczki, D. Ondercin, R. W. Kreilick, Low-temperature NMR studies of a single crystal of trans-Cu(DL-al)\textsubscript{2}H\textsubscript{2}O. J. Am. Chem. Soc. 101 (1979) 2880–2884. doi:10.1021/ja00505a014

2880

[57] G. Szalontai, R. Csonka, G. Speier, J. Kaizer, J. Sabolovič, Solid-state NMR Study of paramagnetic bist[(alaminate-\textsubscript{2}N,O)copper(II)] and bist-(l-amino (cyclo)alkane-1-carboxylato-\textsubscript{2}N,O) copper(II) complexes: Reflection of stereoisomerism and molecular mobility in 13C and 2H fast magic angle spinning spectra, Inorg. Chem. 54 (2015) 4663–4677. doi:10.1021/acs.inorgchem.5b01974

4663

[58] R. Calvo, EPR measurements of weak exchange interactions coupling unpaired spins in model compounds, Appl. Magn. Reson. 31 (2007) 271–299. doi:10.1007/s00311-006-6261

271

[59] M. A. Hitchman, L. Kwan, L. M. Engelhardt, A. H. White, P. W. Anderson, A mathematical model for the narrowing of spectral lines by exchange or motion, J. Phys. Soc. Jpn. 9 (1954) 4899. doi:10.1143/JP23.9.4899

4899

[60] M. S. Torikachvili, K. N. Yang, R. Calvo, O. R. Nascimento, H. Uekusa, S. Ohba, T. Tokii, µ-Aqua-bis(\textgreek{p}-trichloroacetato-O:O')(3-cyanopyridine)(trichloroacetato)copper(II) dichloroform solvate, Acta Crystallogr. C 51 (1995) 625–627. doi:10.1107/S0108270194008579

625

[61] B. Bleaney, K. D. Bowers, Anomalous paramagnetism of copper acetate, Proc. R. Soc. A, London 214 (1952) 451–465. doi:10.1098/rspa.1952.0181

451

[62] C. Kittel, Introduction to Solid State Physics, 8th Edition, Wiley, New York, 2005.

[63] K. Fabricius, U. Lòw, K. H. Mütter, Complete solution of the two dimensional antiferromagnetic Heisenberg model on small lattices, Phys. Rev. B 44 (1991) 9981–9988. doi:10.1103/PhysRevB.44.9981

9981

[64] E. W. Montroll, Theory of the vibration of simple cubic lattices with nearest neighbor interactions, in: Proc. Third Berkeley Symp. Math. Stat. Probab., University of California Press, Vol. III, 1956, pp. 209–246.

[65] M. J. Hennessy, C. D. McBee, P. M. Richards, Effect of interchain coupling on electron spin resonance in nearly one-dimensional systems, Phys. Rev. B 7 (1973) 930–947. doi:10.1103/PhysRevB.7.930

930

[66] O. A. Starikikh, A. W. Sandvik, R. R. P. Singh, Dynamics of the spin-1/2 Heisenberg chain at intermediate temperatures, Phys. Rev. B 55 (1997) 14953–14967. doi:10.1103/PhysRevB.55.14953

14953

[67] T. Oguchi, A. Honma, Theory of ferro- and antiferromagnetism by the method of Green functions, J. Appl. Phys. 34 (1963) 1153–1160. doi:10.1063/1.1729412

1153

[68] P. W. Anderson, New approach to the theory of superexchange interactions, Phys. Rev. 115 (1959) 2–13. doi:10.1103/PhysRev.115.2

2

[69] P. J. Hay, J. C. Thibault, R. Hoffmann, Orbital interactions in metal dimer complexes, J. Am. Chem. Soc. 97 (1975) 4884–4899. doi:10.1021/ja00850a018

4884

[70] O. Kahn, Dinuclear complexes with predictable magnetic properties, Angew. Chemie, Int. Ed. 24 (1985) 834–850. doi:10.1002/anie.198508341

834

[71] P. R. Levstein, H. M. Pastawski, J. L. D’Amato, Tuning the through-bond interaction in a two-center problem, J. Phys. Condens. Matter 2 (1990) 1781–1794. doi:10.1088/0953-8984/2/7/009

1781

[72] M. B. Maple, Low temperature specific heat of Cry-Con grease, Cryogenics 23 (1983) 52–54. doi:10.1016/0011-2275(83)90139-X

52

[73] J. Inorg. Chem. 25 (1986) 4692–4698. doi:10.1021/ic00246a021

4692

[74] E. W. Montroll, Evidence for hydrogen-bond-mediated exchange coupling in an aqua-bridged Cu\textsuperscript{II} dimer: Synthesis, magnetic study and correlation with density functional calculations, Eur. J. Inorg. Chem. 2006 (2006) 329–333. doi:10.1002/ejic.200500709

329