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Synthesis, crystal structure, magnetic properties and DFT calculations

of a mononuclear copper(II) complex: relevance of halogen bonding for

magnetic interaction

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Dedicated to the memory of Cassiano P. Silva.

1. Abstract

The synthesis, crystal structure, magnetic properties and DFT calculations of a new mononuclear copper(II) complex containing a pyrazole-based ligand reported. are In the crystal structure of the [CuCl₂L₂] complex (L = Ethyl 5-amino-1-(4-methoxyphenyl)-1Hpyrazole-4-carboxylate), a network of hydrogen bonds connects the molecular units in the crystal packing. The magnetic studies revealed predominant antiferromagnetic interactions among molecular units. Since there are multiple intermolecular contacts that can act as pathway for magnetic interactions, DFT calculations revealed the fundamental role of N-H^{...}Cl short intermolecular contacts in magnetic behavior. Supported by DFT calculation, the magnetic data above 7.0 K was modeled as a regular Heisenberg chain $(H = -2J \sum_{i=1}^{n-1} \vec{S}_{A_i} \cdot \vec{S}_{A_{i+1}})$ resulting in a weak magnetic coupling constant (J)of -2.6 cm⁻¹. Below this temperature, an unusual magnetic behavior for mononuclear copper(II) complexes was observed: divergence between zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibilities and magnetic hysteresis cycles at low temperatures attributed to spin canting along the chain.

Keywords: copper(II), pyrazole ligands, magnetic properties, spin canting, DFT calculations

2. Introduction

Mononuclear copper(II)-based coordination compounds have been extensively studied in molecular magnetism area, mainly applied as building blocks aiming to obtain a large variety of homo- or heterometallic systems varying from discrete complexes to coordination polymers with different framework topologies [1,2]. The use of ligands able to provide a supramolecular pathway through hydrogen bonding [3] or halide-halide interactions [4] may be important to promote stronger magnetic interactions among mononuclear complexes in the crystal packing. In fact, a strong magnetic interaction of -163 cm^{-1} through halide—halide short contact has been reported [5] showing the importance of this kind of interaction for the magnetic behavior. In addition, copper(II) mononuclear complexes have been used to obtain magnetic ladders [6] which have particular interest due to their relevance for superconductivity and Haldane systems [7,8]. For instance, some of us reported the magnetic properties of the [CuCl₂(paba)₂] compound (paba = *p*-aminobenzoic acid), which behaves as a magnetic chain due to Cu⁻ Cl short contact in the crystal packing [3]. Interestingly, at low temperatures, this mononuclear complex exhibits magnetic hysteresis and divergence between ZFC and FC magnetic susceptibilities attributed to a weak ferromagnetism through the intermolecular hydrogen-bonding pathway between the molecular entities.

More recently, a new burst of interest in mononuclear coordination compounds arose because of its potential application as spin qubits in quantum computation due to long coherence times at high temperatures [9]. In fact, a long coherence time was obtained for a distorted square planar mononuclear copper(II) complex at room temperature [10].

Several $[CuX_2L_2]$ mononuclear systems containing nitrogen heteroaromatic ligands (L) have been reported so far, where X stands for a halogen [11,12]. Among these ligands, pyrazole whose derivatives are well known by their biological activities, are very appealing, since its architecture can be tuned by several substituents, as reported previously [13–15].

Herein, we report the synthesis, crystal structure and magnetic properties of a new mononuclear copper(II)-based complex [CuCl₂L₂] obtained through the reaction between CuCl₂ and Ethyl 5-amino-1-(4-methoxyphenyl)-1*H*-pyrazole-4-carboxylate (L). Magnetic hysteresis was observed at low temperatures as well as separation between ZFC and FC curves. DFT calculations were used to give a theoretical insight about the relevant pathways for magnetic interactions.

SCY

2. Experimental

2.1 –General

Reagents and solvents were purchased from Sigma-Aldrich and used without further purification. The infrared spectrum was recorded on an Alpha-Bruker spectrometer in the range of 4000–500cm⁻¹. The ¹H-NMR spectrum was obtained using a Varian model Unity Plus spectrometer operating at 300 MHz. Magnetic measurements were performed on a Cryogenic SX-600 SQUID magnetometer. The sample was placed in a gelatin capsule and data were corrected for the diamagnetic contribution of the sample and sample holder.

2.2 – Preparation of the ethyl 5-amino-1-(4-methoxyphenyl)-1H-pyrazole-4-carboxylate (L):

The ligand was prepared following the procedure described in the literature [16]. To a mixture of 4-methoxyphenylhydrazine (9 mmol, 1.24 g) dissolved in 10 mL of boiling ethanol was added slowly a solution of ethyl (ethoxymethylene)cyanoacetate (9 mmol, 1.52 g) in 10 mL of ethanol. The reaction medium was refluxed for 20 min. Then, the mixture was poured into 50 mL of ice-cold water. The precipitate was collected by filtration and washed with water. Yield: 1.58g (83%). Mp: 151-153 °C. IR (KBr. cm⁻¹): 3400–3140; 2995; 2912; 1677; 1621; 1552; 1528; 1280; 781–697.¹H-NMR (300 MHz, CDCl3, δ ppm): 7.72 (s, 1H), 7.36 (d, J= 8.9 Hz, 2H), 6.95 (d, J= 8.6 Hz, 2H), 5.13 (br, 2H), 4.23 (q, J= 7.1 Hz, 2H), 1.29 (t, J= 7.1 Hz, 3H).

$2.3 - Preparation of the [CuCl_2L_2] compound$

An ethanolic solution (10 mL) of CuCl₂.2H₂O (1.1 mmol, 18.7 mg) was added slowly to a solution of L (2.2 mmol, 57 mg) dissolved in 10 mL of ethanol under constant stirring. The resulting solution was filtered to remove insoluble material, and then stored at 8 °C. Black crystals obtained after a week were washed with cold ethanol and dried opened to air. Yield: 26 mg (36 %). IR (ATR, cm⁻¹): 3463(w), 3357(w), 3295(w), 3006(w), 2969(w), 2935(w), 2904(w), 2840(w), 1678(m), 1615(m), 1587(w), 1547(m), 1510(m), 1463(w), 1408(w), 1331(m), 1300(w), 1103(m), 1044(w) and 781(w). Anal. Calc. for C₂₆H₃₂Cl₂CuN₆O₇: C, 46.26; H, 4.77; N, 12.45%. Found: C, 46.45; H, 4.29; N, 12.34%. ~

2.4 - X-ray diffraction

The crystallographic data for [CuCl₂L₂] were collected on an Enraf Nonius Bruker KAPPA CCD diffractometer, using graphite monochromatic Mo K α radiation ($\lambda = 0.71069$ Å). Final unit cell parameters were determined fitting all reflections using DIRAX [17]. Collected reflections were integrated using the EVALCCD program [18]. Empirical multi-scan absorption corrections using equivalent reflections were performed with the SADABS program [19]. The structure solution and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-2014 programs, respectively [20]. All atoms except hydrogen were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. The water lattice molecules and carbon atoms of one ester group are disordered and atom occupancies were refined. The displacement parameters of disordered carbon atoms were constrained to be the same using the EADP. Details of data collection and structure refinement for $[CuCl_2L_2]$ are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

	Empirical formula	$C_{26}H_{30}Cl_2CuN_6O_7$
	Formula weight	675.04 g mol ⁻¹
	Temperature	293(2) K
	Wavelength	0.71073 Å
	Crystal system	Monoclinic
	Space group	<i>P</i> 2 ₁ / <i>c</i>
	Unit cell dimensions	a = 9.5046(6) Å
		b = 23.2192(15) Å
		c = 14.8496(9) Å
		$\beta = 90.445(3)^{\circ}$
	Volume	3277.0(4) Å ³
	Z	4
	Density (calculated)	1.368 Mg/m^3
	Absorption coefficient	0.88 mm ⁻¹
	F(000)	1436
	Theta range for data collection	4.11 to 25.12°.
	Index ranges	-11<=h<=11,
		-27<=k<=25,
		-17<=l<=17
	Reflections collected	10149
	Independent reflections	5845 [R(int) = 0.0201]
	Refinement method	Full-matrix least-squares on F^2
	Data / restraints / parameters	5664 / 2 / 406
	Goodness-of-fit on F ²	1.05
	Final R indices [I>2sigma(I)]	R1 = 0.057, wR2 = 0.156
	R indices (all data)	R1 = 0.071, wR2 = 0.170
-	Largest diff. peak and hole	0.68 and -0.74 e.Å

Table 1:	Crystal	data and	structure	refinement	for	$[CuCl_2L_2].$
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2.5 - DFT calculations

Since multiple pathways are presumably reasonable for magnetic interactions, DFT calculations were used to give a theoretical insight about the main pathways for the magnetic couplings. The first-principles bottom-up (FBPU) [21] procedure was applied following the four systematic steps described below:

(1) **Build models consisting in pairs of monomers:** These models were built based on the identification of reasonable Cu^{...}Cu distances and/or intermolecular short contacts that could lead to relevant magnetic interactions;

(2) Calculate the magnetic coupling constant (*J*) for all models: The strength and nature of the *J* was calculated using the Heisenberg-Dirac-van-Vleck Hamiltonian $\hat{H} = -2J\hat{S}_A\hat{S}_B$, where $\hat{S}_A = \hat{S}_B$, and J is calculated as the difference between energies of the triplet (E_{HS}^T) and singlet (E_{BS}^S) states using Eq. 1 [22]:

$$J = -\frac{\left(E_{HS}^{T} - E_{BS}^{S}\right)}{S_{max}(S_{max}+1)} \quad (Eq. 1),$$

The open-shell singlet E_{BS}^{S} is computed using the *broken-symmetry* (BS) procedure [23] in the UKS/TPSS [24] DFT level of theory as implemented in the ORCA 3.0.3 [25] software. The basis sets Def2-TZVP was used for copper(II) ion and Def2-SVP [26] for the remaining atoms. The calculated energies and J have an accuracy of 10^{-8} au (~ 0.002 cm⁻¹).

(3) Determination of the magnetic topology and the finite minimal magnetic model in the crystal: the magnetic topology is straightforwardly defined by looking at the spin centers that make the non-negligible J_{AB} interactions. When |J| < 0.01 cm⁻¹ the magnetic interaction can be considered as negligible. Once the magnetic topology of the crystal is defined, the minimal magnetic model consists of the smallest group of molecules whose replication along the three crystallographic axes reproduces the magnetic topology of the infinite crystal [27].

(4) **Calculation of the macroscopic magnetic properties**: the results accessed by the calculations performed on step 2 support the magnetic model used to fit the data, allowing to build a spin Hamiltonian consistent with the spin topology. This is particularly necessary for the mononuclear system because the magnetic interactions are weak and provided by intermolecular interactions, being quite hard, without the theoretical support, to unambiguously define the main pathways.

3. Results and Discussion

3.1 – Structure description

The compound crystallizes in the $P2_1/c$ space group and the asymmetric unit contains one [CuCl₂L₂] mononuclear complex and one crystallization water molecule. The molecular unit of the complex is shown in Figure 1. The copper(II) ion is *trans*-coordinated by two chloride ions and two pyrazolyl nitrogen atoms (N1 and N4) in a monodentate mode. The definition of the coordination environment of the copper(II) ion was based on the calculation of τ_4 , which is the parameter for evaluating the metal ion geometry of four-coordinate coordination compounds (Eq. 2).

$$\tau_4 = \frac{360^0 - (\alpha + \beta)}{141^0}$$
 (Eq. 2)

In Eq. 2, α and β stands for the two largest angles in the coordination environment. If $\tau_4 = 1$ the geometry is perfectly tetrahedral, while with $\tau_4 = 0$ a square-planar geometry is observed [28]. The obtained value of τ_4 is 0.406 indicating that the coordination environment is intermediate between the square-planar and tetrahedral geometry. The observed Cu-N and Cu-Cl bond lengths are typical in the comparison to similar complexes previously reported [29].



Figure 1: The asymmetric unit of the $[CuCl_2L_2]$. Thermal ellipsoids are at 40% of probability. Crystallization water molecules, hydrogen atoms and part of the disordered carbon atoms from ester group were omitted for the sake of clarity (color codes: gray: carbon; red: oxygen; blue: nitrogen, green: chlorine and ciano: copper).

Bond lengths	Bond angles			
Cu1–Cl1	2.2321(12)	N1-Cu1-Cl1	91.82(9)	
Cu1–Cl2	2.2158(11)	N1-Cu1-Cl2	151.03(11)	
Cu1-N1	1.991(3)	N4-Cu1-Cl1	151.80(11)	
Cu1-N4	2.002(3)	N4-Cu1-Cl2	91.55(9)	
		Cl1-Cu1-Cl2	95.51(5)	
		N1-Cu1-N4	95.11(12)	

Table 2: Selected bond length (Å) and bond angles (°) for [CuCl₂L₂]

The ester and amino substituents in the 4 and 5 positions of the pyrazole ring play an important role in the crystal packing of the complex due to the establishment of intra- and intermolecular hydrogen-bondings, as depicted in Figure 2. Each [CuCl₂(L₂)] unit interacts in different ways with adjacent molecules; the first interaction (I) involves a pair of carboxylic groups and amine $[N6^{--}O5^i =$ 2.985(4)Å], while the second one (II) is between the carboxylic and amino groups $[O1^{...}N6^{ii}]$ 3.023(5)Å] (Symmetry codes: (i) -x+3, -y, -z+1; (ii) x, -y+1/2, z-1/2) (Figure 2a). The intermolecular distances between the copper(II) ions involved in the pair I is 14.503(9)Å, whereas in II is 10.491(8) Å. The I and II intermolecular interactions lead to a supramolecular chain running along the b axis, as highlighted in Figure 2b. Furthermore, short contacts $Cl^{...}H-C_{sp2}$ [Cl2...C11ⁱⁱⁱ =3.772(4) Å] and N-H^{...}Cl [N3^{iii...}Cl1 = 3.824(5) Å, H3a^{...}Cl1 = 3.046; \angle N3-H3a^{...}Cl1 = 151.4°, iii=1+x, y, z] are observed in the crystal packing (Figure 2c) leading to a third pair of molecules featuring a Cu^{...}Cu distance of 9.5046(9) Å. The distances between the acceptor and donor atoms related to the N-H^{...}Cl short contacts are slightly larger when compared with other systems previously reported [30,31], however importance of this contact will be discussed below, supported by Quantum Theory of Atoms in Molecules calculations (QTAIM). Hydrogen bonds between water crystallization molecules and chlorine or amine groups also contributed to stabilize the crystal packing $(O3w^{-1}N3 =$ 2.886(14) Å and O2w^{···}Cl1^{iv} = 3.123 (12), iv = -x+2, y+1/2, -z+3/2).



Figure 2: (a) Details of the crystal packing of $[CuCl_2L_2]$ showing the network of hydrogen-bonding involving the oxygen and nitrogen atoms from ester and amine groups, respectively. (b) Supramolecular zig-zag chain running along the *b* crystallographic axis. (c) Short contacts Cl^{...}H-C_{*sp*2} and N-H^{...}Cl along the *a* axis.

3.2 – Magnetic measurements

The temperature dependence of the $\chi_M T$ product and χ_M are shown in Figures 3 and S1, respectively. The $\chi_M T$ value at room temperature is 0.43 cm³.K.mol⁻¹, which is consistent with a paramagnetic copper(II) ion (g=2.15). Upon cooling, this value remains constant until c.a. 150 K and decreases continuously to 0.33 cm³.K.mol⁻¹ at 7 K due to the presence of antiferromagnetic interactions. Interestingly, a peak is observed in the $\chi_M T$ curve, reaching a maximum of 0.35

cm³.K.mol⁻¹ at 5.4 K, suggesting a small spin canting which gives a small increment of the magnetic moment (weak ferromagnetism). Below to 5.4 K, $\chi_M T$ value continues to decrease to 0.28 cm³.K.mol⁻¹ at 2.8 K due to the antiferromagnetic interaction. The reciprocal susceptibility versus temperature data (T > 70 K) were fitted to the Curie-Weiss law, affording a Curie and Weiss constants of 0.44 cm³.mol⁻ ¹ and -3.4 K, respectively. The negative Weiss constant evidences weak antiferromagnetic coupling among the spin carriers provided by intermolecular interactions. As discussed previously, a network formed by hydrogen-bondings and short contacts lead to multiple possible pathways for intermolecular magnetic interactions. In this case, to model the overall magnetic behavior is quite complicated. On the other hand, DFT calculations were successfully used to give theoretical insight about relevant pathways for magnetic interaction [32]. A careful analysis of the crystal packing of [CuCl₂L₂] showed a supramolecular chain running along the crystallographic axis a through N-H^{...}Cl and C-H^{...}Cl short contacts (Figure 2c), and DFT calculation showed that the magnetic interaction is relevant only through this pathway (see below). Thus, to estimate the magnetic interaction a regular 1D Heisenberg model $(H = -2J \sum_{i=1}^{n-1} \vec{S}_{A_i} \cdot \vec{S}_{A_{i+1}})$ was used to fit the magnetic data in the temperature range 7 to 290 K using the following empirical expression that reproduce Bonner Fisher's numerical calculation, eq. 3, [33,34]:

$$\chi_M T = \frac{Ng^2 \beta^2 [0.25 + 0.14995x + 0.30094x^2]}{k[1 + 1.9862x + 0.68854x^2 + 6.0626x^3]}$$
(Eq. 3)

where x = |J|/kT

The equation 3 is able to describe the magnetic data in temperature range 7-290 K with g = 2.20 and |J|/k= 3.68(5) K (2.6 cm⁻¹) (solid line – Fig. 3), revealing a weak antiferromagnetic coupling between the copper(II) ions in the supramolecular chain. This weak value is of the same order as other copper(II)-based mononuclear systems in which the magnetic interactions were mediated by intermolecular short contacts [29].



Figure 3: Temperature dependences of $\chi_M T$ product (circles) and ${\chi_M}^{-1}$ (square) at 1000 Oe. Solid lines represent fits of the magnetic data (see text for details). Dotted line below 10 K is an extrapolation of the calculated curve.

The 1D model fails to reproduce the magnetic data below 7 K as shown by dotted line that represents an extrapolation of fitted curve. This deviation can be due to other magnetic interactions. Thus, a mean field approximation was tried to take into account the interchain magnetic interaction, however no satisfactory result could be achieved. Similar magnetic behavior observed for $[CuCl_2(paba)_2]$ [3] was attributed to weak ferromagnetic interchain magnetic interactions mediated by N-H⁺ Cl short contacts. Nevertheless, in the $[CuCl_2L_2]$ compound the weak ferromagnetic interaction is more pronounced even at an applied field of 1000 Oe. A magnetic irreversibility below 6.5 K was observed in the ZFC-FC magnetic susceptibilities (Fig. 4a), being more apparent in the measurement performed at lower magnetic field. Contrary to the $[CuCl_2(paba)_2]$ compound, the $[CuCl_2L_2]$ molecules within the supramolecular chain are not related by an inversion symmetry operation. This weak ferromagnetism arises from spin canting due to non zero antisymmetric exchange [35,36]. The

magnetization versus field curves at 1.8 K and 4 K in the field range of 0–65 kOe are shown in Fig. S2 (ESI). The magnetic field of 65 kOe is not able to override the magnetic interactions at these temperatures and the saturation of the magnetization is not reached. The magnetization value of 0.71 N μ_B at 65 kOe is smaller than the value saturation 1.1 N μ_β expected for a S=1/2 with g = 2.20 consistent with antiferromagnetic interactions obtained previously. Hysteresis cycles were observed at 1.8 and 4.0 K. Figure 4b shows details of the hysteresis loop at 4.0 K, which presents a small coercive field of 11 Oe.



Figure 4: ZFC (black) and FC (red) magnetic susceptibilities at 10 Oe (a). Detail of the hysteresis loop at 4.0

K (b).

3.3 – DFT calculations

Single-point calculations performed on the UKS TPSS/Def2-TZVP//Def2-SVP level of theory showed that the spin population generated by the single unpaired electron in the [CuCl₂L₂] monomer is shared between the metal center and the atoms directly coordinated to it (Figure 5a). The higher spin density (0.46) is localized over the copper(II) ion, as expected, and its atomic orbitals have the highest contribution to the formation of the Singly Occupied Molecular Orbital (SOMO) (Figure 5b). Each chloride has approximately 0.21 and nitrogen atoms present approximately 0.05 of the total spin

density. Magnetic interactions between monomers are mainly dependent on the overlap between SOMO-SOMO orbitals of the molecules. The orbital density depicted in Figure 5b strongly suggests that relevant interactions are involving the chloride ions since they have high spin density.



Figure 5: (a) Spin density (isosurface 0.03 a.u., depicted in yellow) with copper in cyano and chlorine in green. (b) SOMO orbital for $[CuCl_2L_2]$ (positive and negative phases are represented as white and blue, respectively with isosurface of 0.03 a.u.).

The careful analysis of the crystal structure using FPBU suggested that four symmetry-unique Cu^{...}Cu distances (d_i) were presumably assumed as relevant magnetic pathways for interaction. They were chosen due to shortest distances between highest magnetic spin density centers (copper(II) ions) with distances ranging from 6.8560(7) Å in d₁ to 14.503(9) Å in d₄ (Figure 6). Although d₄ is quite long, we included it to explore the role of the hydrogen-bonding as a pathway.



Figure 6: Geometries of the unique Cu^{\cdots}Cu pairs selected in the FPBU procedure. Distances are d₁ = 6.8560(7), d₂ = 9.5046(9), d₃ = 10.491(8) and d₄ = 14.503(9) Å.

Calculated *J* values (Table 3) for all selected pairs using the broken-symmetry approach showed that only d₂ (Figure 6) has a non-negligible antiferromagnetic coupling constant of -7.56 cm⁻¹. This value is higher than the experimental one obtained by fitting the data using the Heisenberg chain model (J = -2.6 cm⁻¹). As highlighted in Figure 2c, the strongest magnetic coupling found for $J_{(d2)}$ gives rise to supramolecular chains running along the *a* axis.

d_i	d(Cu-Cu) /Å	$[\operatorname{CuCl}_2\operatorname{L}_2] J(cm^{-1})$	$[CuBr_2L_2] J(cm^{-1})$
d1	6.856	0.01	0.06
d2	9.505	-7.56	-18.79
d3	10.491	~0	-0.03
d4	14.503	~0	-0.37

Table 3: Comparison of calculated J for [CuCl₂L₂] and for [CuBr₂L₂]

The magnitude of the calculated magnetic exchange (*J*) for d₂ is consistent with that observed for other compounds, in which the magnetic coupling is intermediated through intermolecular hydrogen bonds [37]. Such hydrogen bonding in the d₂ pair involves the chloride and NH₂ group of adjacent monomers. Additional analysis of this intermolecular interaction was performed using a **QTAIM** calculation [38–40] and the results revealed a point in the space where the first derivative of the electron density was equal to zero, the so-called *bond critical point* (BCP). This BCP confirms the existence of the N-H⁻⁻Cl interaction between the adjacent monomers (Fig. S3- ESI). QTAIM results comply with the Poincaré-Hopf relation [41], adding to the confidence that all critical points for this system have been found and that a relevant intermolecular interaction takes place.

A subsequent analysis to confirm the importance of the hydrogen bonding to the $J_{(d2)}$ magnetic coupling constant was carried out by changing the chloride ion by another halogen (Br⁻). To assure the reliability of the $J_{(d2)}$, an approximated model was built based on the data obtained for the crystal structure of [CuCl₂L₂], but replacing Cl⁻ for Br⁻. Cu-Br bond lengths of 2.38 Å were used for the calculated [CuL₂Br₂] molecule based on the average value reported for tetracoordinated mononuclear copper(II) complexes (51 structures) in the Cambridge Structural Database [42] (see Fig. S4), considering two nitrogen atoms and two bromide ions as donors. The other bond lengths and bond

angles were kept the same as for $[CuL_2Cl_2]$. This approximated model agrees with the crystal structure reported for isostructural copper(II) complexes coordinated by Cl⁻ or Br⁻ ions that bond lengths (except for Cu-halogen), bond angles and torsion angles as well as intermolecular distances are nearly the same [43,44]. The calculated $J_{(d2)}$ showed that larger halogen anions increase the antiferromagnetic exchange between molecules (Table 4) and analysis of the spin population (0.39 for Cu, 0.31 for Br and 0.05 for N) confirms that delocalization of the spin density is favored for larger halogen ion. As observed for [CuCl_2L_2], the magnetic interactions through d₁, d₃ and d₄ are also very small when compared with the interaction through d₂, emphasizing the relevance of the latter magnetic pathway. In fact, larger magnetic coupling constants were observed for other isostructural complexes coordinated to bromide when compared with chloride [6,42].

A spin canting due to antisymmetric magnetic interaction is possible and observed for systems where the interacting magnetic units are not related by inversion symmetry operation [45]. Although the center of inversion prevents the antisymmetric exchange, compounds that crystallize in centrosymmetric space groups exhibiting spin canting have been reported, since the interacting magnetic units were not related by aforementioned symmetry operation [46]. A careful analysis of the crystal structure of [CuCl₂L₂] shows that the monomeric units are related by the symmetry operation inversion through d1 and d4 pathways, so no antisymmetric interaction would occur; therefore, a canting of spins should not happen. This is in agreement with the obtained result that the magnetic interaction through d₂ pathway (not related by center of inversion) is more relevant for the overall magnetic behavior.

Conclusions

In this work, we present the synthesis, crystal structure and magnetic properties of a new mononuclear copper(II) complex. Intra- and intermolecular interactions involving amine, ester and chloride groups play an important role to the crystal packing and these interactions can act as

pathways for the magnetic interactions between the copper(II) ions. The magnetic studies showed that $[CuCl_2L_2]$ behave as 1D Heisenberg chain through short NH^{...}Cl contacts between monomers. At low temperatures, weak ferromagnetic interactions and magnetic hysteresis observed are due to spincanting along the chain. The absence of an inversion center between the mononuclear units in the supramolecular chain leads to the observed antisymmetric exchange. A careful analysis of the intermolecular magnetic pathways supported by DFT calculations confirms the relevance of short contacts for this unusual magnetic behavior.

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Supporting information:

The Supporting Information contains the thermal dependence of χ_M and the fit using Eq. S1 (Fig. S1); Field dependence of magnetization at 2.0 and 4.0 K (Fig. S2), QTAIM analysis list (Fig. S3) and the statistical analysis performed using the CCDC database for mononuclear copper(II)-bromide complexes (Fig. S4). CCDC-1831274 contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Synthesis, crystal structure, magnetic properties and DFT calculations of a mononuclear copper(II) complex: relevance of halogen bonding for magnetic interaction

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Research Highlights

- Mononuclear copper(II) compound containing a pyrazol-based ligand.
- Short contact N-H...Cl plays a key role to the magnetic properties.
- Magnetic hysteresis and divergence between ZFC-FC curves.
- Spin canting phenomena.