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Synthesis, crystal structure, magnetism and specific heat of a new copper(II) compound with *p*-aminobenzoic acid

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ABSTRACT

In this work we present the synthesis, crystal structure, magnetic and specific heat measurements of a new monomeric copper(II) compound, in which the metal ion is coordinated to two *p*-aminobenzoic acid (PABA) molecules and two chloride ions. This compound with formula $[CuCl_2(C_7H_7NO_2)_2]$ presents a peculiar crystalline structure packing, showing hydrogen-bonds between carboxylic acid groups and short N-H···Cl contacts resulting in a polymeric character in two dimensions. In the third direction, Cu···Cl close contacts between neighboring molecules are responsible for a chain-like magnetic behavior. Considering the simplicity of the molecular unit, the magnetic properties show surprising results: below 6.4 K a hysteresis cycle appears in the magnetization curves as well as a splitting between low field ZFC-FC measurements. No phase transition to a long-range order was observed by specific heat measurement. © 2011 Elsevier B.V. All rights reserved.

1. Introduction

Several strategies have been used to synthesize molecule-based magnetic compounds [1–3], among which the assembly of metal ions and organic molecules is the most popular. Monomers, dimers, trimers or more complex structures with magnetic dimensionalities greater than zero, such as chains, planes and three dimensional systems can be obtained depending on the choice of the organic ligand. The magnetic properties of these compounds are strongly correlated with the crystal structure, which is essential to understand the possible ways in which the magnetic coupling occurs [4]. Covalent bonds are not the only possible pathways for these magnetic couplings; weak intermolecular interactions have also been considered a key to understand and explain the magnetic behavior in molecular compounds [5–7]. Chemists can modify these intermolecular interactions by using different ligands and molecular moieties [8–11].

Many examples of coordination compounds with general molecular formula $[CuX_2(L)_2]_n$, where *L* stands for an amine ligand and *X* for a halide ion are known [12–14]. They have been studied

because copper(II) is the simplest transition magnetic metal ion, which can be theoretically treated by S = 1/2 Heisenberg models, such as one- and two-dimensional structures with ferromagnetic or antiferromagnetic interactions [15-17]. Magneto-structural correlations in these compounds highlighted the importance of hydrogen bonds and the halide-halide interactions for the understanding of the magnetic properties [18]. The p-aminobenzoic acid (PABA) is a well known and versatile ligand which can generate intermolecular interactions through hydrogen bonds and $\pi - \pi$ stacking interactions. In addition, different coordination compounds have been obtained as result of its ability to coordinate either by carboxylate or amine groups [19-21]. In this work we present the synthesis, crystalline structure, magnetic and specific heat measurements of a new copper(II) complex with molecular formula $[CuCl_2(C_7H_7NO_2)_2]$, which displays unusual magnetic properties for this class of coordination compounds.

2. Experimental

2.1. General

Anhydrous $CuCl_2$ and PABA ($C_7H_7NO_2$), methanol and absolute ethanol were purchased from commercial sources and used without further purification. Elemental analysis (CHN) was carried out in a Perkin–Elmer CHN 2400 spectrometer. Infrared spectrum





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was recorded from KBr pellets in 4000–500 cm⁻¹ range on a Spectrum One Perkin–Elmer spectrometer.

2.2. Synthesis of [CuCl₂(C₇H₇NO₂)₂]

To a solution of *p*-aminobenzoic acid (222 mg, 16.2 mmol) in 25 mL of absolute ethanol, CuCl₂ (105 mg, 0.79 mmol) was added slowly under constant stirring. The color of the solution changed from pale yellow to green and a dark-brown microcrystalline precipitate appeared. The reaction mixture was left under constant stirring for 2 h. The precipitate was isolated by filtration and washed with cooled absolute ethanol. Ten milligrams of the microcrystalline powder were dissolved in 15 mL of methanol and through slow evaporation, single rhombohedra crystals were obtained. Yield: 196 mg (61% based on copper chloride). Selected IR data (cm⁻¹): 3438 (ν O–H), 3254 and 3142 (ν N–H), 1808 (ν C=O) and 1606, 1580, 1512 (ν C=C). Anal. Calc. for C₁₄H₁₄Cl₂Cu-N₂O₄: C, 41.28; H, 3.47; N, 6.88. Found: C, 41.45; H, 3.63; N, 6.82%.

2.3. X-ray diffraction data

Single-crystal X-ray measurements were carried out on a Bruker KAPPA CCD diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The final unit cell parameters were determined from all reflections obtained with DIRAX program [22]. The integration of the collected reflections was performed using the EVALCCD program [23]. The absorption correction using equivalent reflections was performed with the SADABS program [24]. The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages, respectively [25]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms. Crystallographic data and processing parameters are given in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1

Summary of the crystal	structure, data c	ollection and re	finement for	[CuCl ₂ (PABA) ₂].
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Empirical formula	$C_{14}H_{14}Cl_2CuN_2O_4$		
Formula weight (g mol ⁻¹)	408.71		
T (K)	298(2)		
Wavelength (Å)	0.71073		
Crystal system	triclinic		
Space group	ΡĪ		
Unit cell dimensions			
a (Å)	4.6719(7)		
b (Å)	5.9916(4)		
c (Å)	14.0625(13)		
α (°)	86.942(7)		
β (°)	88.683(11)		
γ (°)	88.115(9)		
V (Å ³)	392.72(7)		
Ζ	1		
Calculated density (Mg m ⁻³)	1.728		
Absorption coefficient (mm ⁻¹)	1.75		
F(000)	207		
θ Range for data colletion (°)	3.63-27.5		
Index ranges	$-6 \leq h \leq 6, -7 \leq k \leq 7,$		
	$-18 \leqslant l \leqslant 17$		
Reflections collected	5138		
Independent reflections (R _{int})	1780 (0.041)		
Data/restraints/parameters	1780/0/106		
Goodness-of-fit (GOF) on F^2	1.05		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.033$, $wR_2 = 0.076$		
R indices (all data)	$R_1 = 0.049, \ wR_2 = 0.099$		
Largest difference peak and hole (e Å ⁻³)	0.34 and -0.33		

For $[CuCl_2(PABA)_2]$, $w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 0.1659P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2

Selected bond distances (Å) and bond angles (°) for [CuCl₂(PABA)₂].

Bond lengths		Bond angles	
Cu1–N1 Cu1–N1 ⁱ Cu1–Cl1 Cu1–Cl1 ⁱ	2.044(2) 2.044(2) 2.2645(7) 2.2645(7)	N1-Cu1-N1 ⁱ N1-Cu1-Cl1 N1 ⁱ -Cu1-Cl N1-Cu1-Cl1 ⁱ	180.00(10) 88.62(7) 191.38(7) 91.6(3)
Hydrogen bonds (D–H· O1–H1···O2 ⁱⁱ O1···O2 ⁱⁱ N1–H1b···Cl1 ⁱⁱⁱ N1···Cl1 ⁱⁱⁱ	···A) 1.82 2.631(3) 2.62 3.510(2)	Cl1-Cu1-Cl1 ⁱ O1-H1…O2 ⁱⁱ N1-H1b-Cl1 ⁱⁱⁱ	180.0 172.2 170.5

Symmetry codes: (i) -x + 1, -y + 1, -z + 1; (ii) -x + 3, -y + 2, -z; (iii) -x + 1, -y + 2, -z + 1.

2.4. Magnetic measurements

Magnetization curves versus temperature or applied field were measured using a Cryogenic SX-600 SQUID magnetometer on 27.2 mg of a polycrystalline sample. Zero-field cooled (ZFC) and field cooled (FC) were performed between 2.5 and 300 K. The sample was placed in a gelatin capsule and data were corrected for the diamagnetism and sample holder. Ac susceptibility measurements were carried out in a Quantum Design PPMS (Physical Properties Measurement System) model 6000 with frequencies ranging between 10 Hz and 10 kHz and constant magnetic field of 12 Oe.

2.5. Specific heat measurement

Heat capacity measurements were performed by using a microcalorimeter probe of a PPMS (Physical Properties Measurement System made by Quantum Design), for temperatures in the range 1.8–30 K at zero applied magnetic field. 2.1 mg of the sample was mixed to 2.0 mg of Apiezon N-grease and attached to the calorimeter. This procedure is necessary to improve the sample-calorimeter thermal contact. The heat capacity of the sample was then obtained by properly subtracting the addenda (calorimeter plus Ngrease) heat capacity [26].

3. Results and discussions

3.1. Structure description

The structure of [CuCl₂(PABA)₂] is shown in Fig. 1. The copper(II) ion lies in a square planar environment, coordinated to nitrogen atoms from two trans PABA molecules and two chloride ions. The Cu-N1 and Cu-Cl1 bond lengths are typical when compared with other complexes containing amine and chloride ligands [16,17,27]. The bonds angles N1-Cu-N1' and C11-Cu-C11' are 180°. Each [CuCl₂(PABA)₂] molecule is linked to another one through hydrogen bonds between their carboxylic groups, leading to a hydrogen-bonded layer. The bond lengths $H1\cdots O2$ and O1...O2 (Table 2) are slightly longer than similar supramolecular synthons of double hydrogen-bonded carboxylic groups [28-30]. The carboxylic groups are important to the structural packing of the compound, being responsible for a polymeric character established by units linked by pairs of hydrogen bonds. In addition, weak interactions between hydrogen and chloride of neighboring molecules lead to a two dimensional network. The H1b...Cl1 distance and N1-H1b. Cl1 bond angle are similar to others described in the literature [21,31,32].

The shortest distance between copper(II) ions is 4.672 Å, determined by a translation operation over the a axis (Fig. 2a). At this point, it is important to highlight that chloride and copper(II) ions



Fig. 1. ORTEP view of the molecular unit of compound [CuCl₂(PABA)₂]. Ellipsoids are at 50% probability.



Fig. 2. Crystal packing of [CuCl₂(PABA)₂]: (a) ---- intermolecular interaction between chloride and copper(II) ions. (b) Hydrogen bond and weak interactions N-H…Cl.

from neighboring molecules are separated by a distance of 3.563 Å, which is too long to be considered a di- μ -chloro bridge [27,33]. The copper ions are separated by a distance of 5.992 Å along the *b* axis, where the molecular units are connected by weak N–H···Cl intermolecular interactions (Fig. 2b). The longest one, through the hydrogen bonds formed by the carboxylic acid group is 17.596 Å. The dihedral angle between the equatorial plane containing the copper ion and the *p*-aminobenzoic acid phenyl ring is 69.23°. All planes of the phenyl rings are quasi parallel to each other, with a centroid distance between molecular units of 4.667 Å.

3.2. Magnetic properties

3.2.1. DC magnetic measurements

The thermal dependence of the $\chi_M T$ product measured with an applied field of 1000 Oe (0.1 T) is shown in Fig. 3. In the temperature range 280–100 K, $\chi_M T$ has a constant value of 0.37 cm³ K mol⁻¹, as expected for a paramagnetic $S = \frac{1}{2}$ ion, with g = 2.00 (0.375 cm³ K mol⁻¹). Upon cooling, the $\chi_M T$ value decreases indicating the presence of antiferromagnetic interactions between the copper ions. Between 15 and 8 K a "shoulder" appears



Fig. 3. Thermal dependence of $\chi_M T$ product measured at H = 1 kOe. The solid line is the best fit by Eq. (1). Inset: plot of $\chi_M T$ vs. *T* in temperature range 2–35 K.

(inset Fig. 3) and below that the $\chi_M T$ value decreases continuously to zero, suggesting an antiferromagnetic ground state.

In compound $[CuCl_2(4-Et(py))_2]$ (4-Et(py) = 4-ethylpyridine) [34], chloride ions from neighboring molecules occupy the outof-plane positions above and below the square quadratic plane with a distance of 3.22 Å. Due to the out-of-plane stacking, the compound was considered a chloride-bridged 1D linear chain. In $[CuCl_2(PABA)_2]$, the copper environment presents the same characteristics, with the distance between chloride and copper(II) ions of 3.563 Å along the *a* axis (Fig. 2a), which is slightly longer than in $[CuCl_2(4-Et(py))_2]$. Therefore, considering a regular chain 1D Heisenberg model, with Hamiltonian $H = -2J\sum_{i=1}^{n-1}S_{A_i} \cdot S_{A_{i+1}}$, we used the following empirical expression that reproduce Bonner Fisher's numerical calculation [35,36] to fit the magnetic data of $[CuCl_2(PABA)_2]$:

$$\chi T = \frac{Ng^2\beta^2[0.25 + 0.14995x + 0.30094x^2]}{k[1 + 1.9862x + 0.68854x^2 + 6.0626x^3]} \tag{1}$$

where x = |J|/kT.

This 1D model describes the magnetic data in the fitted temperature range 280–15 K (solid line – Fig. 3) with the best fit leading to $|I|/k = 4.9 \text{ K} (3.4 \text{ cm}^{-1})$ and Landée factor of 2.02. The coupling constant value is of the same order of magnitude when compared with those obtained for chloride-bridged 1D linear chain analogs of general molecular formula $[CuX_2(L)_2]$ (L is a ligand containing the amine function) [32]. The fitted $\chi_M T$ curve was extrapolated below 15 K and shows clearly that this 1D model is not enough to describe the low temperature data, where other magnetic interactions have to be taken into account. We thus tried to use a first-order molecular field correction [12] to account for the magnetic path through the short contact between H1b...Cl1 (Fig. 2b). No acceptable fit could be obtained below 15 K. This unusual behavior becomes more apparent when the field cooled (FC) magnetization measurement is carried out under a lower magnetic field (30 Oe), as shown in Fig. 4, displaying an increase in the $\chi_{\rm M}T$ value around 8 K. In addition the low field zero field cooled (ZFC) and FC magnetization curves show a magnetic irreversibility, below the maximum at 6.4 K (Fig. 5a). The irreversibility between the ZFC-FC curves decreases when the magnetic field intensity was increased from 20 to 100 Oe (Fig. S1, Supplementary information). As expected, this compound also displays a hysteresis cycle in the range ±250 Oe at 1.8 K (Fig. 5b), suggesting a ferromagnetic like behavior. Spin canting and the related weak ferromagnetism [37] could also



Fig. 4. Thermal dependence of $\chi_M T$ product measured at H = 30 Oe.

explain the results but is ruled out by the presence of an inversion center between the copper(II) ions [38,39].

The deviation of the experimental results with $\chi_{\rm M}T$ values above the 1D chain behavior suggests that ferromagnetic interactions between copper(II) ions of neighboring chains are present. The enhancement of the observed behavior in low field suggests that these interactions should be weak. Ferromagnetic interchain coupling is expected by considering H1b…Cl1 short contact in the *b* direction, as shown in Fig. 6. It is important to emphasize that the magnetic coupling between copper ions separated by the molecular synthons was neglected due to the large distance between these ions (~17 Å). It is clear that the full description of the magnetic properties cannot be explained by a simple 1D or 1D plus mean field corrections models.

3.2.2. AC magnetic measurements

The alternating current magnetic susceptibility of $[CuCl_2(PA-BA)_2]$ compound presented a peak at the same temperature as the low field magnetization (~6.4 K) that does not change with frequency. The out-phase component (χ'') is very small with small increase below 7 K (Fig. S2, Supplementary information). There is a weak frequency dependence on both components below 7 K. These results indicated that $[CuCl_2(PABA)_2]$ compound does not present slow magnetization relaxation or glassy behavior as found on single molecule magnets or single chain magnets [40], but suggest some kind of ordering.

3.3. Specific heat

The specific heat versus T data showed a continuous increase without any sharp peak that would indicate a phase transition to a long range order as suggested by the AC magnetic measurements (Fig. S3, Supplementary information). The overall specific heat data showed a T-dependence that is described by a lattice term and a magnetic contribution. Unfortunately we could not synthesize a nonmagnetic analog compound by substitution of copper(II) by zinc(II), so it was not possible to determine the lattice specific heat beyond the Debye approximation. Therefore we used this approximation cautiously, and the 1D Heisenberg chain model, with $H = -2J\sum_{i=1}^{n-1}S_{A_i} \cdot S_{A_{i+1}}$, to calculate the specific heat in the temperature range 8–15 K using Eq. (2). The magnetic contribution in Eq. (2), $c_{mag}(T)$, is a polynomial expression that reproduces the Fabricius' numerical calculations [41,42]. The term LT^3 in Eq. (2) is the lattice contribution to the total specific heat in the Debye approximation.



Fig. 5. (a) ZFC and FC measures performed under applied field of 20 Oe. (b) Hysteresis cycle at 1.8 K in magnetic field range ±250 Oe.

(2)



Fig. 6. Spin topology in [CuCl₂(PABA)₂] compound.

 $c(T) = c_{mag}(T) + LT^3$

with

$$c_{mag}(x) = R\left(\frac{x + Ax^2 + Bx^3}{3 + Cx + Dx^2 + Ex^3 + Fx^4 + Gx^5}\right)$$

where

x = kT/|J|

and the A-G parameter values were obtained from Ref. [41].

The results are shown in Fig. 7, where it can be seen that the 1D chain model accounts for the data reasonably in the temperature range 8–15 K. The best fit was achieved with |J|/k = 11.1 K (7.7 cm⁻¹), which is higher than the obtained from magnetic data. The lattice contribution term, from which we estimated the Debye temperature $\theta_D = 78 \text{ K}$, was $L = 4.1 \text{ mJ mol}^{-1} \text{ K}^4$. This value is of the same order as previously reported for a similar mononuclear copper(II) compound [43]. Inset in Fig. 7 represents the magnetic contribution, obtained by subtracting the lattice contribution from total specific heat. The calculated c_{total} was extrapolated below 8 K and an excess contribution becomes apparent, attributed to other interactions not taken into account by this simple 1D model.

4. Conclusion

In this work we presented the synthesis, structure, magnetic and specific heat measurements of the [CuCl₂(PABA)₂] compound. Intermolecular interactions act as pathways for the main magnetic



Fig. 7. Temperature dependence of total specific heat of $[CuCl_2(PABA)_2]$ (open circles). Dash-dot and solid lines represent the lattice contribution and the fit by Eq. (2), respectively. Dashed line is the extrapolated 1D behavior below 8 K. Inset: magnetic contribution to total specific heat.

interactions between copper(II) ions and can be modeled, in first approximation, by a 1D Heisenberg antiferromagnetic chain model. At low temperatures, a deviation from this model and an unusual magnetic irreversibility was observed, suggesting the presence of weak ferromagnetic interactions. No phase transition was evidenced by specific heat measurements, but an excess contribution due to additional interactions is responsible to the deviation from a simple chain model as also seen in the magnetic measurements. Further work such as EPR, X-ray diffraction at low temperature and simulation should be pursued in order to explain the observed low temperature behavior.

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Appendix A. Supplementary material

CCDC 784624 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Figure S1 displays ZFC and FC measures performed under applied field of 100 Oe. The temperature dependence of in-phase and out-phase components of the ac susceptibility are shown in Figure S2. The thermal dependence of total specific heat is depicted in Figure S3. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2011.08.035. These data include MOL files and InChiKeys of the most important compounds described in this article.

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