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Experimental and theoretical investigation of structure-magnetic properties relationships in a new heteroleptic one-dimensional triple bridged azido/acetato/DMSO copper (II) coordination polymer

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Abstract:

We report the synthesis, structure, and magnetic investigation of a novel one-dimensional copper (II) coordination polymer: formula $[\text{Cu}(\mu_{1,1}\text{-N}_3)(\mu_{1,3}\text{-OAc})(\mu\text{-DMSO})]_{\infty}$ (**1**) (OAc=acetate). The connection between neighbouring copper ions arises through a triple bridge involving *EO* type azide, *syn-syn* carboxylate and μ -DMSO molecule in apical positions forming an elongated octahedral coordination of copper ions. Magnetic susceptibility measurements show that complex (**1**) exhibits ferromagnetic intrachain interactions $J_{\text{chain}} = +66 \text{ cm}^{-1}$ whereas a metamagnetic behaviour occurs below 2.1 K related with antiferromagnetic inter-chain interactions with a critical field of 600 Oe at 1.8 K. DFT calculations were carried out to rationale the in-chain ferromagnetic interactions between copper ions. We found that the

ferromagnetic coupling between copper ions is less sensitive to variation of bond length and/or Cu-N-Cu angle that may be caused by external stimulus such as temperature or pressure.

Keywords: One-dimensional coordination polymer; Triple-bridged-Cu (II); Carboxylate; Azide; Molecular magnetism.

1. Introduction

Structural architecture and magnetic properties of coordination polymers are presently of considerable interest [1-3]. In particular, the advancements in the realm of low-dimensional magnetic coordination polymers, as single-molecule magnets [4-7], single-chain magnets [8-10], and others displaying low-dimensional magnetic characteristics such as metamagnetism [11, 12] contributed to the advent of new concepts in magnetism and nanoscience, with the support of theoretical and experimental developments. Much research in this field is not only focused at trying to explain the theory behind experimental phenomena, but also to develop and synthesize new magnetic materials [13, 14]. A key step in the logical design of coordination polymers is the control of the interconnections between metal centers. This fosters to rational designing of different structural motifs influencing the chemical properties of materials such as metal-organic frameworks (MOFs) [15, 16] or metal-organic polyhedra (MOPs) [17, 18]. In this sense, the carboxylate unit is widely used in the synthesis of coordination polymers [1, 19], due to their interesting coordination chemistry allowing for unusual structural features and leading to various physical and chemical properties and practical applications as dyes, extractants, drugs, pesticides, catalysts, etc [19-22]. In addition to transmitting magnetic exchanges and binding to metal clusters or chains, carboxylates may also turn the metal centred building units into aesthetically pleasing structures [16, 19]. Coordination with carboxylates is quite versatile and antiferromagnetic, ferromagnetic or metamagnetic materials have been prepared, based on this ligand [23-26]. Similarly, the azido ligands are able to link metal ions in different coordination modes, which induces a rich structural diversity and leading to different magnetic properties in azido-metal complexes [13, 27, 28]. Actually, the azido-based copper (II) complexes get a lot of interest in the steadily growing literature on molecular magnetism [29-31]. Hence, combining azide and carboxylate in one compound is an interesting approach to construct new magnetic systems, due to the versatility of these ligands in both coordination chemistry and magnetochemistry [14, 32-35]. Due to variety of possible combinations, there remains a need for investigating new mixed ligand compounds allowing to understand better the impact of such multiple bridging on structure and magnetism variations,

especially in Cu^{II} azido / carboxylate systems [33-35]. In this context, the present work reports on a new 1D Cu (II) coordination polymer involving a mixed azido / carboxylato / DMSO triple-bridge between metal centres. We report the synthesis, the structure and magnetic properties of a novel one-dimensional coordination polymer with the formula [Cu($\mu_{1,1}$ -N₃)($\mu_{1,3}$ -OAc)(μ -DMSO)]_∞. The structure-property analysis is supported by DFT calculations. This one-dimensional system exhibits a ferromagnetic interaction between neighbouring Cu (II) ions within chains. The chains couple antiferromagnetically, and a metamagnetic behaviour is observed below T_N = 2.1 K.

2. Experimental

2.1. Materials and methods

All chemicals were commercially available reagent grade and used without further purification. Elemental analyses (C, H, N, S) were performed at the ‘Service de Microanalyses’ of the Institut de Chimie de Strasbourg (Université de Strasbourg, France). FT-IR spectra, in the region 400–4000 cm⁻¹, were recorded on a FT-IR Spectrum 2 Perkin Elmer. Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance diffractometer employing Cu K α_1 radiation (λ = 1.54056 Å). Magnetic measurements were performed using a Quantum Design SQUID-VSM magnetometer. Susceptibility was measured in an applied field of 1 kOe and isothermal magnetization was performed at 1.8 K in magnetic field of \pm 0-70 kOe. AC susceptibility measurements were carried out in 3.5 Oe – 83 Hz alternative field. Diamagnetic corrections were estimated from Pascal’s constants.

2.2. Synthesis of the complex

2.2.1. Synthesis of [Cu(OAc)($\mu_{1,1}$ -N₃)(μ -DMSO)]_∞ (**1**)

1 mmol of sodium azide was added slowly to a solution of CuCl₂.2H₂O (1 mmol, 0.1704 g) in 5 mL EtOH. The reaction mixture was stirred for 10 min while 1 mL acetic acid was added dropwise. The mixture was stirred at room temperature for 30 minutes, after several days well-shaped green needle crystals of (**1**) were obtained, filtered, washed with cold water and dried in an oven at 40 °C. Anal. Calc for C₄H₉CuN₃O₃S, C: 19.79; H: 3.73; N: 17.31; S: 13.21%. Found: C: 19.92; H: 3.45; N: 17.53; S: 12.94%.

2.3. X-ray diffraction studies

A green crystal of (**1**) was mounted on micro loops for data collections. The X-ray single-crystal data of compound (**1**) was collected on a Bruker-AXS APEX II CCD diffractometer at 298(1) K. The crystallographic data, conditions retained for the intensity data collection and main

features of the structure refinements are listed in Table 1. The intensities were collected with Mo K α radiation ($\lambda = 0.71073$ Å). Data processing, Lorentz-polarization and absorption corrections were performed using APEX2 [36], and the SADABS computer programs [37]. The structure of (1) was solved by direct methods and refined by full-matrix least-squares methods on F^2 , using the SHELXL-2018/3 program package [38]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. Molecular plots were performed with the ATOMS and Crystal Maker programs [39–40]. Selected bond lengths and angles are given in the Table S1. Table S2 in the Supporting Information, lists of the hydrogen bond interactions for (1). Geometrical calculations were carried out with PLATON [41] and PARST [42].

Table 1: *Crystal data and structure refinement data for $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$*

Empirical formula	C ₄ H ₉ CuN ₃ O ₃ S
Formula weight	242.74
Crystal system	Tetragonal
Space group	<i>I</i> 4/m
<i>T</i> (K)	298(1)
<i>a</i> (Å)	16.924(5)
<i>b</i> (Å)	16.924(5)
<i>c</i> (Å)	6.464(5)
$\alpha = \beta = \gamma$ (°)	90
<i>V</i> (Å ³)	1851.4(18)
<i>Z</i>	8
ρ_{calc} (g/cm ³)	1.742
μ (mm ⁻¹)	2.558
Crystal size (mm ³)	0.12 × 0.11 × 0.05
Radiation	MoK α ($\lambda = 0.71073$)
2θ range for data collection (°)	6.748 to 59.278
Index ranges	-22 ≤ <i>h</i> ≤ 22, -23 ≤ <i>k</i> ≤ 23, -6 ≤ <i>l</i> ≤ 8
Reflections collected	5348
Independent reflections	1409 [$R_{\text{int}} = 0.0296$, $R_{\text{sigma}} = 0.0286$]
Data/restraints/parameters	1409/0/76
Goodness-of-fit on F^2	1.149
Final <i>R</i> indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0420$, $wR_2 = 0.0922$
Final <i>R</i> indexes [all data]	$R_1 = 0.0706$, $wR_2 = 0.1000$
Largest diff. peak/hole / e Å ⁻³	0.31/-0.39

2.4. Computational Details:

All computations are performed using the density functional theory [43, 44], as implemented in the SIESTA code [45]. We used the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof (PBE) parametrization [46]. The core electrons were treated with norm-conserving Troullier-Martin pseudopotentials [47] and the valence charge density was expanded over a numerical orbital basis set, including double-zeta polarized functions. The real space mesh grid of an equivalent cut-off of 400 Rydberg have been used. The copper chain was simulated by considering a tetragonal structure with $a = b = 20 \text{ \AA}$ while $c = 6.464 \text{ \AA}$. The large in plane lattice parameter ensures that there is no interchains interactions.

It is known that, in the presence of transition metal-oxides, the local density approximations usually fails to describe the ground state properties as well as the magnetic configurations and in order to improve the LDA, we used the atomic self-interaction correction (ASIC) method [48] implemented in the transport code Smeagol [49] to verify the results obtained with the SIESTA.

3. Results and Discussion

3.1. Crystal and molecular structure of $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$ (**1**):

Single-crystal X-ray structure analysis revealed that complex (**1**) crystallizes in the tetragonal space group $I4/m$ (N° 87) and exhibits infinite linear polymeric chains. The structure of the chains is represented in figure 1 with atom labelling. In the asymmetric unit of (**1**), there is one Cu (II) ion, a half acetato ligand, one coordinated DMSO molecule and one azido ligand. Cu (II) ions lies on a crystallographic inversion centre (0.75, 0.25, 0.25), while the azido anion and the two carbon atoms of the acetate lies on mirror planes ($Z = \frac{1}{2}$). The C3, S1 and O2 atoms from the DMSO molecule lie on a mirror plane ($Z = 0$). The coordination sphere of each Cu (II) ion contains four oxygen atoms ((O1, O1^{iv}) from acetate ligand, (O2, O2^{iv}) from DMSO molecule) and two nitrogen atoms (N1 and N1ⁱ) from azide ligand. In addition, the hexacoordinated Cu (II) ion is surrounded by N_2O_4 atoms. The connection between the metallic centre is ensured by acetate ligand with a *syn-syn* $\eta^1 \eta^1: \mu_2$ carboxylate bridging mode, an azido anion in the *end-on* type bridging mode and a μ -O atom of the coordinated DMSO molecule. This yields to a formal 1D chain along the crystallographic c -axis (figure 2). This kind of linkage has been previously reported with different co-ligands [50-55].

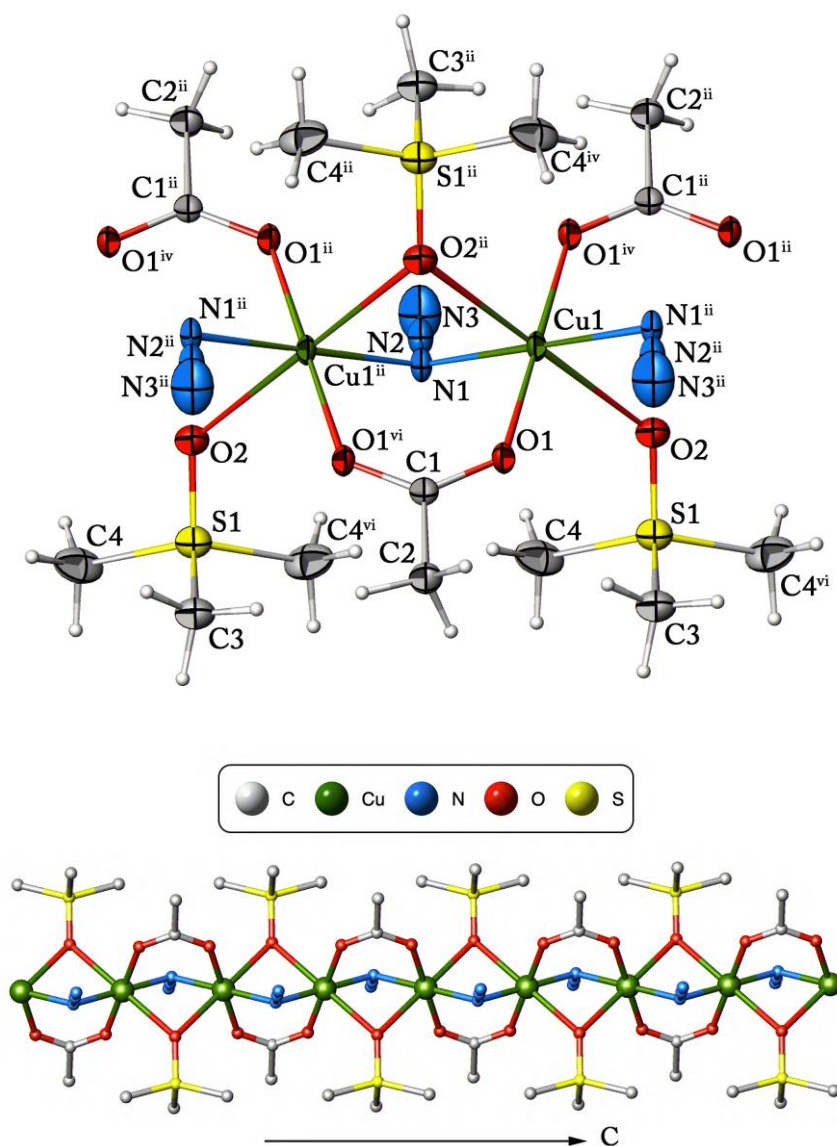


Figure 1. Top: ORTEP view of $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$, 50% probability level.

Bottom: The 1D chain with mixed acetato, azido and DMSO oxygen bridges for $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$. Symmetry codes: (i) $-x+3/2, -y+1/2, -z+3/2$; (ii) $x, y, -z+2$; (iii) $-x+3/2, -y+1/2, z-1/2$; (iv) $x, y, -z+1$

The mean Cu-L bond distance increases in the sequence: 1.954(2) Å ($\mu\text{-O}$ acetic acid), 1.993(2) Å ($\mu_{1,1}\text{-N}$) and 2.557(3) Å ($\mu_2\text{-O}$ DMSO), and it is noteworthy that the axial bond distance is longer than the equatorial. This is due to the typical Jahn-Teller effect. The apical Cu-O2 distance is much longer than normal (2.557 Å) but corresponds to distances observed in the Cambridge structural databases (CSD version 5.43 updates Mar 2022) [33, 55]. Selected bond distances and bond angles are gathered in Table 2. All the Cu-L bond distances are comparable with the corresponding ones observed in literature [29, 56-58].

Two adjacent Cu-L octahedra share edge formed by apical oxygen of DMSO and equatorial nitrogen of azide ligand, with Cu1-O2_{DMSO}-Cu1^v bridge angle of 78.38°. The Cu1-N1_{Azide}-Cu1ⁱⁱ bridge angle of 108.34 (17)° is in normal range of the EO azido bridging mode. The Cu...Cu distance is found to be 3.232 (3) Å within the chains and the shortest metal-metal separation between two chains [8.469 (2) Å] is large, compared with the observed intrachain distances in similar compounds [29, 52]. Azido ions is slightly bent, with N1-N2-N3 angle of 178.09 ° and exhibits unsymmetrical N-N bond lengths, with N(1)-N(2) bonds (N(1)-N(2) = 1.210 (6) Å) significantly longer than N(2)-N(3) = 1.123(7) Å.

In the crystal structure of (**1**), the connection between the chains is ensured by weak C-H...N hydrogen bonding between the C2 carbon of acetate ligand and the terminal nitrogen atom (N3) of azide group of the neighbouring molecule ($-y+1, x, z$), via the hydrogen H2A [C2...N3 = 3.405 (3) Å, \angle C2-H2A...N3= 154.98 °]. These interactions extend the 1D chain structure of (**1**) to a three-dimensional (3D) supramolecular network (figure 2).

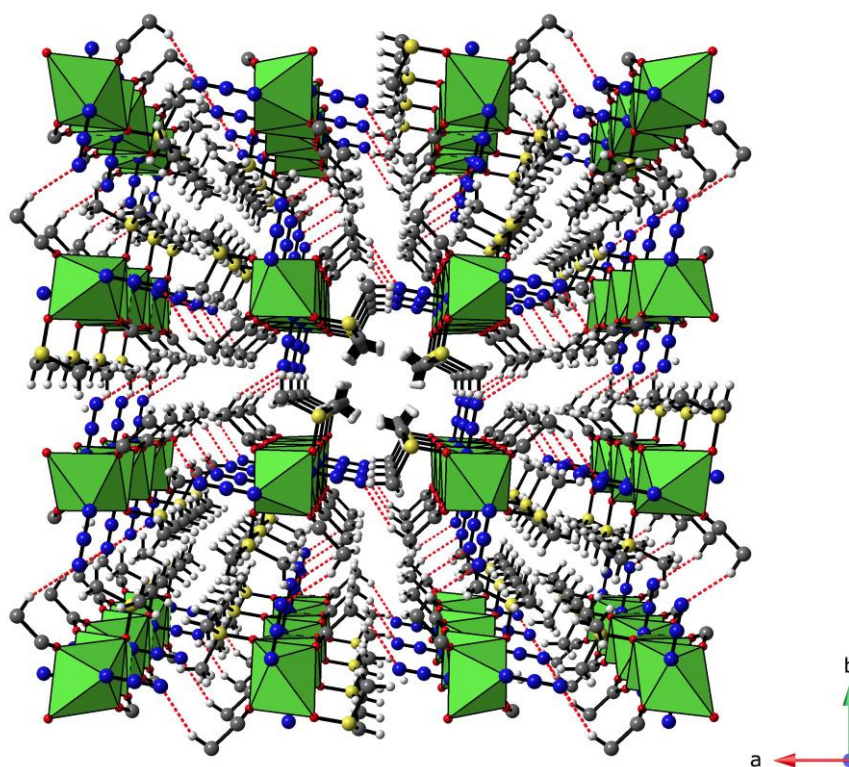


Figure 2. 3D supramolecular network of $[Cu(OAc)(\mu_{1,1}-N_3)(\mu-DMSO)]_{\infty}$ assembled by C-H...N interactions shown by red dashed lines.

3.2. Spectroscopic properties:

The FT-IR spectrum of compound (**1**) (figure 3) was carried out in the field 400-4000 cm⁻¹. The band situated at 619 and 676 cm⁻¹ arise from the stretching asymmetric and symmetric C-S-C

vibration mode, respectively. The asymmetrical valence vibration of the azide gives an intense band at 2088 cm^{-1} , while the band at 1295 cm^{-1} is attributed to $\nu_{\text{sym}}(\text{N}_3)$ in agreement with the **End-On** bridging mode of azido anions. Also, complex **(1)** exhibits the typical acetato vibrations $\nu_{\text{asym}}(\text{COO}^-)$ at 1548 and $\nu_{\text{sym}}(\text{COO}^-)$ at 1418 cm^{-1} . The difference between the two characteristic bands is 130 cm^{-1} indicating a bidentate coordination mode of carboxylate group in keeping with the structural findings [59]. The FT-IR data also show a S=O stretching band at 1023 cm^{-1} . This S=O band shifts to a lower frequency as compared to free DMSO (1055 cm^{-1}), which is consistent with O-coordinated DMSO [60]. Moreover, the large band observed between 2850 and 3000 cm^{-1} is attributed to the symmetrical and asymmetrical stretching vibration of CH_3 groups. Finally, the FT-IR spectra of complex **(1)** show also a broad band around 3300 cm^{-1} who can be attributed to the moisture. The metal ligand vibrations are expected below 500 cm^{-1} .

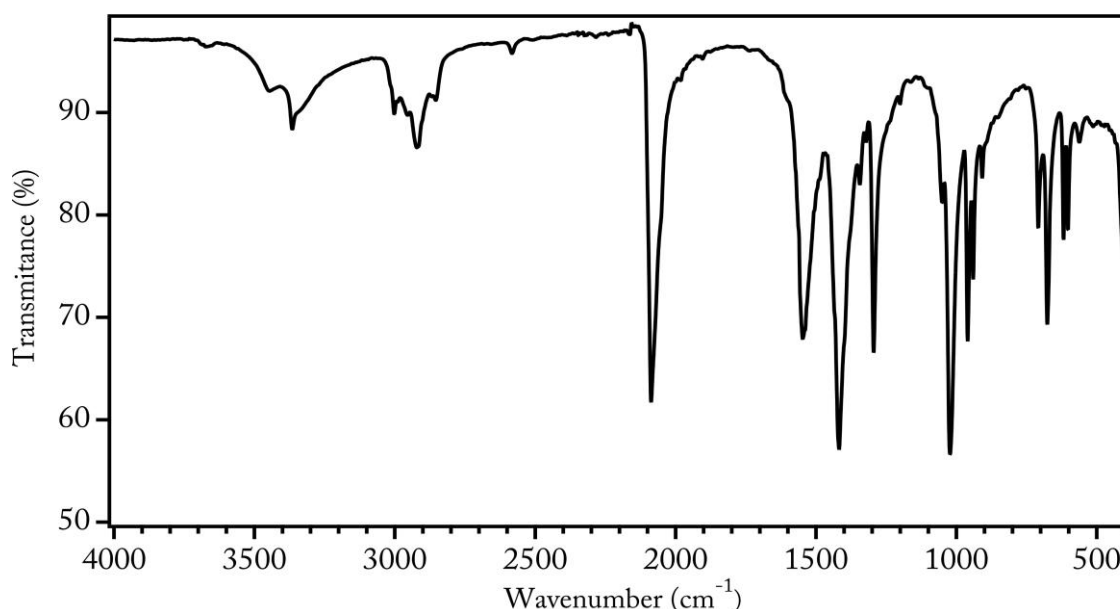


Figure 3. Infrared spectrum of $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$

3.3. Magnetic properties

The purity of phase **(1)** was confirmed by powder X-ray diffraction (PXRD) before magnetic measurement (figure S1). The magnetic properties of $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$ were studied on randomly oriented polycrystalline samples. The variation of the magnetic susceptibility (χ) was recorded in an applied field of 100 Oe within the temperature range 1.9 K – 300 K. The data have been corrected for the diamagnetism of the sample and sample holder. The magnetic susceptibility χ exhibits a steady increase with decreasing temperature up to a maximum of 2.23 emu.mol^{-1} at 2.05 K and a small decrease down to 1.9 K. The inverse

susceptibility vs temperature plot is presented in supplementary materials (Figure S2). Above 175 K, the curve is linear and was fitted to the Curie-Weiss law, $\chi = \frac{Ng^2\mu_B^2}{3kT} S(S+1)$, with $S = 1/2$, leading to $g = 2.207(2)$ and $\theta = +59.0(4)$ K. The g factor value is in keeping with usual values observed for Cu (II) ions which range between 2.0 and 2.3 [61]. The quite large and positive value of the Weiss temperature indicates ferromagnetic interactions, whereas, the deviation to higher values suggests the occurrence of an antiferromagnetic contribution at lower temperatures. Accordingly, the value of the χT product of **(1)** at ambient temperature is $0.57 \text{ emu.K.mol}^{-1}$ which exceeds the spin-only value of $0.375 \text{ cm}^3\text{.K.mol}^{-1}$ for $S = 1/2$ ion base on $g = 2.0$. Upon cooling, the χT vs T curve increases until it reaches a maximum of $5.3 \text{ emu.K.mol}^{-1}$ at 2.70 K, which suggests dominant ferromagnetic interactions between copper (II) ions within the chains. Then, the value of χT decreases slightly to reach $4.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.9 K (figure 4).

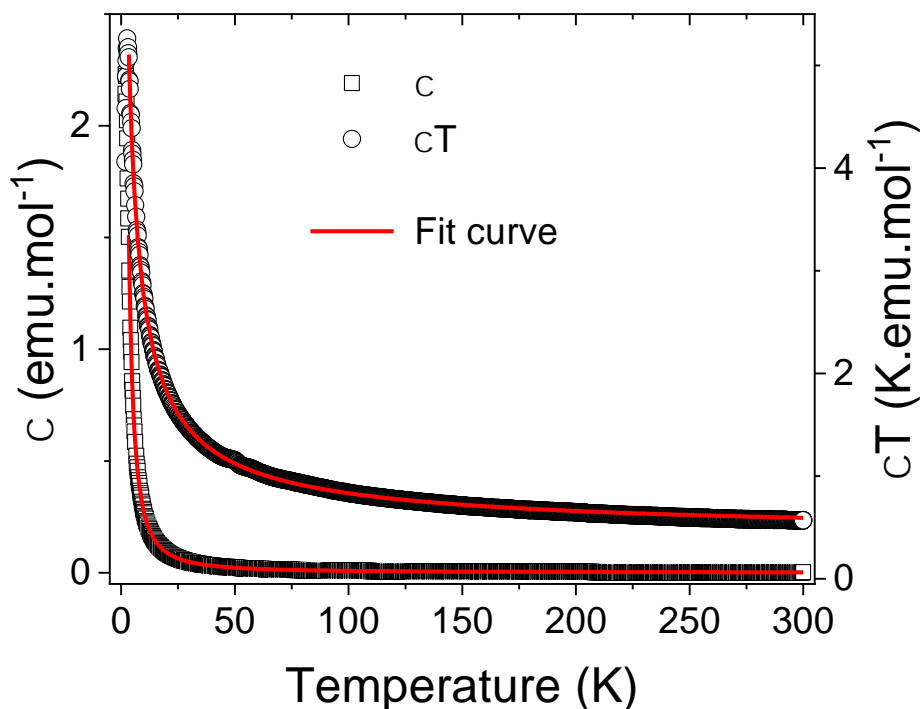


Figure 4. Magnetic susceptibility χ and χT product variation as a function of temperature measured in a field of 100 Oe for $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$.

The red solid lines correspond to the best fit of the data using the high temperature series expansion for Heisenberg $S=1/2$ chain model. (See text)

Alternating field susceptibility measurements also indicate the presence of a maximum of $\chi'(T)$ at $T_N = 2.1$ K, while no signal is being recorded in the imaginary part of the susceptibility (figure S3). This whole behaviour indicates a long-range antiferromagnetic order below 2.1 K, which means the ferromagnetic chains are antiferromagnetically coupled together by a weak

antiferromagnetic interaction. This interpretation is confirmed by the magnetization curve recorded at 1.8 K (figure 5), which has a sigmoidal shape, characteristic of a metamagnetic transition with a threshold field of 600 Oe. The threshold field necessary to overcome the antiferromagnetic interaction between chains is defined by the inflection point in the magnetization curve.

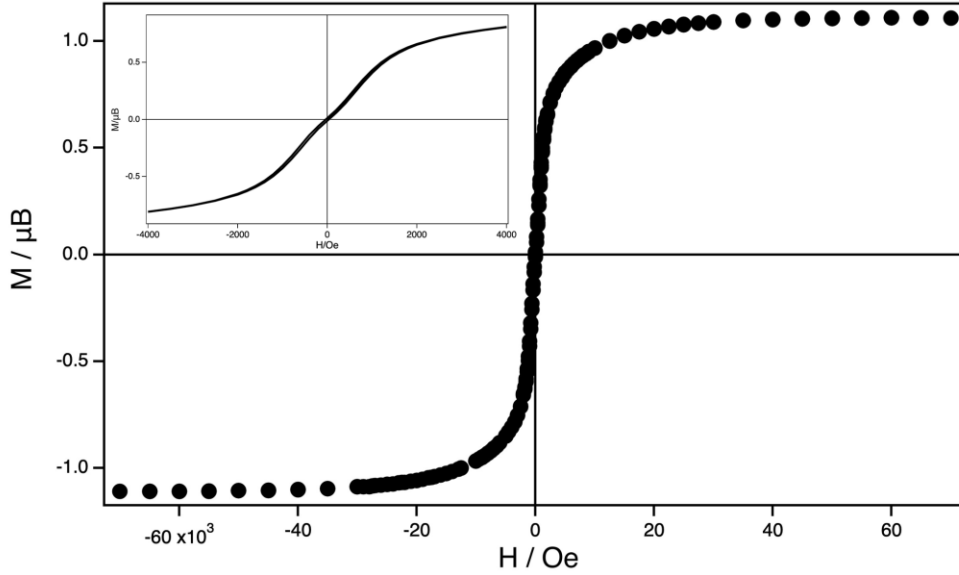


Figure 5. Magnetization curve of $[Cu(OAc)(\mu_{1,1}-N_3)(\mu-DMSO)]_{\infty}$ at $T=1.8$ K

When the magnetic field is increased beyond the threshold field, the moments of the neighbouring chains are aligned and the magnetization continues to increase until reaching a saturation value of about $1.06 \mu_B$ which is a normal value for one spin $S = \frac{1}{2}$ (figure 5). To compute the exchange interaction strength (J) between the Cu (II) centres along the chains, the magnetic susceptibility data were fitted using the analytical expression proposed by Baker *et al.* [62]. for Heisenberg $S = \frac{1}{2}$ ferromagnetic chains based on the following spin exchange Hamiltonian:

$$H = -J \sum_{i=1}^{n-1} S_i \cdot S_{i+1}$$

The thermal variation of the molar magnetic susceptibility for chains is then given by the equation:

$$\chi_{ch} = \frac{N\mu_B^2 g^2}{4kT} \left(\frac{N}{D}\right)^{2/3} \quad (1)$$

where : $N = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.8329959y^4 + 14.036918y^5$

$D = 1.0 + 2.7979916y + 7.0086780y^2 + 8.6538644y^3 + 4.5743114y^4$ with $y = J/2kT$. To take into account the influence of the inter chain interaction, j' , we considered a molecular field using the usual expression : [63, 64]

$$\chi = \frac{\chi_{ch}}{1 - \left(\frac{2zj'}{Ng^2\mu_B^2} \right) \chi_{ch}} \quad (2)$$

The above expression allows the evaluation of zj'/k where z holds for the number of neighboring chains interacting with each other with interaction j' . The experimental data were reproduced using the equation (2) for temperatures above T_N , yet we noticed a large uncertainty on the refined values for g , J and zj' , due to high correlation between the three parameters. Such correlation was also reported in similar works on ferromagnetic chains [65, 66]. We thus fixed the g value to 2.207 as deduced from the fit of the inverse susceptibility vs T curve to the Curie-Weiss law. With this constrain on g and fitting together the χ (T) and χT (T) for $T \geq 3$ K we reproduced very well the experimental data, with the best refined values $J/k = +66.04(2) \text{ cm}^{-1}$ and $zj' = -0.042(3) \text{ cm}^{-1}$ (figure 4).

3.4. Magneto-structural correlations

Several pathways are involved in the super exchange along the copper chain: the oxo bridge of the DMSO (Cu-O length of 2.557 Å) with a rather small Cu-O-Cu angle favouring ferromagnetic coupling [67] and the carboxylate bridge with the *syn-syn* conformation, which is known to favour weak antiferromagnetic interactions between neighbouring metal ions [1]. The third way of exchange is the azido bridge with the **End-On** conformation, which is a very efficient magnetic exchange pathway, that results mainly in ferromagnetic interactions [35, 68]. The magnitude of the corresponding exchange constant J depends on several factors. Mainly J depends on the Cu-N-Cu angle, the out-of-plane deviation τ of the azido group (i.e. angle between the azido group and the Cu-N-Cu plane) and the Cu...Cu distance. According to the literature on copper complexes showing similar mixed ligand exchange pathway involving EO-azido coordination mode for Cu (II) ions, ferromagnetic coupling can be found for Cu-N-Cu angle between 101 and 126°. Moreover, large out-of-plane deviation favours ferromagnetic coupling [35, 68]. In the compound (**1**) $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N}_3)(\mu\text{-DMSO})]_{\infty}$, one observes a Cu-N-Cu angle of 108.34 (17)° and a quite high value of $\tau = 30^\circ$ that support the ferromagnetic character of the coupling through the EO azido bridge. The magnetic interaction transmitted between the isolated ferromagnetic chains is afforded by an additional pathway formed by the hydrogen-bonding between the carbon atom of carboxylate ligand and the terminal nitrogen atom

of the azido groups. This interaction is merely responsible for weak antiferromagnetic coupling between the ferromagnetic chains, leading to antiferromagnetic ordering below $T_N = 2.1$ K. Below T_N , a metamagnetic transition is observed for a critical field $H_C = 600$ Oe, which indicates an interchain interaction of few hundredths of cm^{-1} , which is consistent with the value $zj' = -0.04$ cm^{-1} obtained from the fit of the magnetic susceptibility data [69]. To better discern magneto-structural correlations, structural parameters and J coupling constants in similar carboxylato / EO-azido / Cu (II) systems have been summarized in Table 2, where the J value of 66 cm^{-1} of the compound (**1**) falls simply in the coupling range J reported for the corresponding angles. Yet, the analysis of the variation of the J values as a function of $\text{Cu}^{2+} \dots \text{Cu}^{2+}$ distance and Cu-N-Cu angle is not that straightforward, merely due to the occurrence of multiple exchange pathways in (**1**) or in the reference compounds listed in Table 2.

Table 2. Comparison of the structural parameters (distances [\AA] and angles [$^\circ$]) and magnetic interaction (J [cm^{-1}]) for linear Cu^{II} chain based on a triple bridging syn-syn-carboxylato/EO-azido/ μ -O systems

$\text{Cu}^{2+} \dots \text{Cu}^{2+}$ distance (\AA)	Cu-N-Cu ($^\circ$)	J (cm^{-1})	Refcode CSD	Ref
3.154	104.81	40.2	LOHNEE	[34]
3.200	104.65	69.38	HUTGUA	[50]
3.160	105.24	36.2	HOQHOM	[51]
3.192	105.95	59.74	NAZTUG	[70]
3.182	106.05	65.27	VOKKOX	[52]
3.180	106.5	68.94	BIPZEI	[33]
3.190	106.54	126	NOBVEG	[55]
3.204	106.82	67.6	LOHJAW	[34]
3.219	107.58	126	NOBVIK	[55]
3.213	107.1	56.21	BIPZAE	[33]
3.205	107.85	77.94	BIPZIM	[33]
3.232	108.36	66.04	This work	-
3.279	109.37	97.85	MOJLII	[54]
3.291	110.29	81.22	EHEWOE	[71]

3.5. DFT calculations

In order to confirm the ferromagnetic interaction between copper ions in the linear chain, we used the density functional theory [43], as implemented in siesta code [45], to calculate the exchange interaction, within the parametrization of PBE [46] for the exchange-correlation potential. We used a double zeta polarized basis set to describe all atomic orbitals and a mesh cutoff of 400 Rydberg. The double-zeta polarized basis is used to add flexibility to the basis to adjust to different configurations by increasing the radial and orbital flexibilization [72].

The chain is simulated by a tetragonal structure with $a = b = 20$ \AA while $c = 6.464$ \AA (figure S4).

The total energy calculations show that along the chain, the copper magnetic moments are coupled ferromagnetically with an energy difference of 29 meV per pair of copper atoms. This value agrees very well with the fitted value of $J = +66.04 \text{ cm}^{-1}$ which for an assumed spin $\frac{1}{2}$ for copper ions leads to an energy difference of 32.7 meV. We also investigate the variation of the exchange coupling as function of the distance between copper ions by changing the value of c parameter and the results are shown in figure 6. It is clear that the Cu ions coupled ferromagnetically with a variation of about 20% of its value when the distance varies by $\pm 10 \%$.

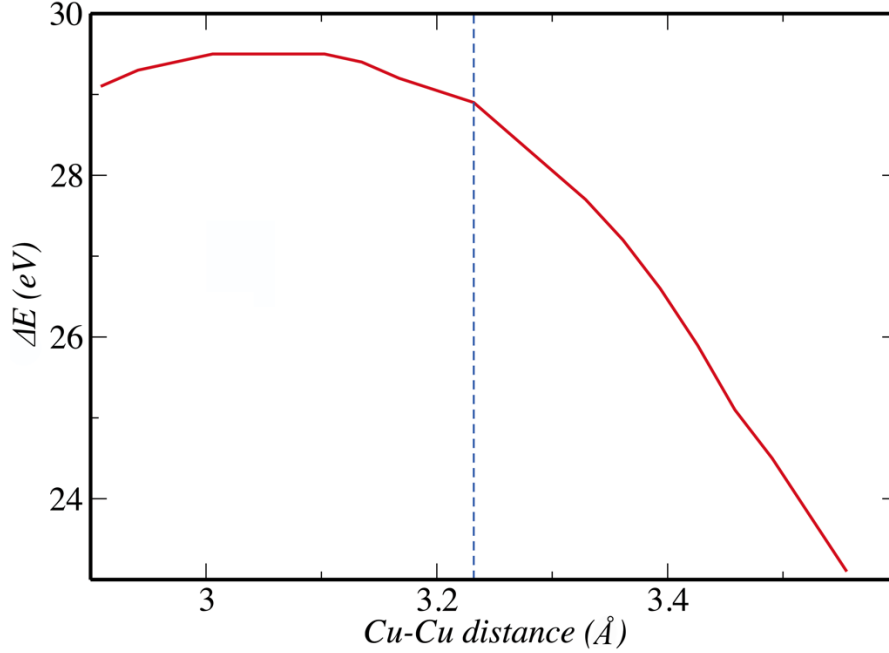


Figure 6. Variation of the total energy difference (ΔE) between the antiferromagnetic and ferromagnetic configuration as function of the distance between copper ions. The horizontal dashed line indicates the experimental Cu-Cu distance.

It is also known that in transition metal-oxides the local density approximations usually fails to describe the ground state properties as well as the magnetic configurations and in order to improve the LDA, we need to correct it either using the LDA+U approach or to include the self-interaction correction [48, 73]. We did perform atomic self-interaction correction (ASIC) [48] calculations and we got the same nature and magnitude of the exchange interaction strength. This means that the ferromagnetic coupling between copper atoms is rather robust against external stimulus such as temperature or pressure.

In order to investigate the geometrical stability of the molecule, molecular geometry was fully optimized without any symmetry constraint at the PBE level until the forces acting on atoms are below 10^{-2} eV/\AA . Two approaches were adopted. First, the size of the cell and its shape are kept fixed with an out-of-plane lattice constant equal to the experimental value ($c=6.464 \text{ \AA}$) while atomic positions are relaxed, and secondly all degrees of freedom (atomic position, size

and shape of crystalline cell) are relaxed minimizing both forces and strains. The calculated distances and angles are reported on table 3 and compared with the experimental values. We calculate also the relative deviation of the calculated value compared to the experimental ones, defined as the ratio of the absolute difference between experimental and theoretical values to the experimental values.

Table 2: *Calculated distances and angles for linear chain $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N3})]_{\infty}$ with Fixed / Relaxed cell compared the experimental values and their relative deviations.*

Distances & angles	Theoretical values	Experimental values	Relative deviations (%)
Cu1-N1	1.995 / 1.997	1.993 (3)	0.1 / 0.2
Cu1-O1	1.951 / 1.954	1.954 (3)	0.15 / 0
N1-N2	1.260 / 1.259	1.206 (7)	4.5 / 4.4
N2-N3	1.172 / 1.173	1.125 (8)	4.2 / 4.3
O1-C1	1.294 / 1.295	1.253 (4)	3.3 / 3.3
C1-CH3	1.53 / 1.526	1.507 (8)	1.5 / 1.3
Cu1-N1-Cu1	108.19 / 103.35	108.36 (17)	0.15 / 4.6
N1-N2-N3	177.17 / 177.19	178.2 (7)	0.6 / 0.6
Cu1-O1-C1	130.01 / 128.66	131.10 (3)	0.8 / 1.8
O1-C1-O1	127.2 / 127.13	127.0 (5)	0.16 / 0.1

We should mention here that if the size is relaxed, we get the same order of magnitude, except the Cu-N-Cu angle which is smaller for relaxed cell. This is due to the smaller lattice parameter $c = 6.268 \text{ \AA}$ compared to the experimental value of 6.464 \AA (a deviation of -3%).

From the above comparison, we can conclude a good agreement between experimental and theoretical values, and that the largest deviation is observed in the N-N bond lengths but it is less than 5%. This deviation may be explained by the absence of DMSO in calculating the atomic positions of linear chain $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N3})]_{\infty}$ while experimental positions are obtained for the whole compound (1) $([\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N3})(\mu\text{-DMSO})]_{\infty})$. Furthermore, once the relaxed structure is obtained, the exchange coupling strength is then calculated and it is of the order of 26 meV. This confirms that the ferromagnetic coupling between copper atoms robust within the linear chain $[\text{Cu}(\text{OAc})(\mu_{1,1}\text{-N3})]_{\infty}$.

4. Conclusion

In conclusion, a novel one-dimensional copper (II) coordination compound based on triple bridging azido/carboxylato/DMSO has been synthesized and structurally characterized, by using single crystal X-ray crystallographic tools. The Cu (II) centers are hexacoordinated and the repeating units of copper ions, act as one-dimensional nodes which are linked through the acetato and azido anions and DMSO molecules to build a 1-D network extending parallel to the

[001] direction. The chains are interconnected and forms a 3-D supramolecular network *via* weak C-H...O interactions. The magnetic measurements of the compound (1), reveal that magnetic interactions within the chains are globally ferromagnetic in nature with an exchange constant of 66 cm^{-1} , while weak antiferromagnetic interchain interactions lead to a 3-D magnetic ordering at $T_N = 2.1\text{ K}$, stabilizing a metamagnetic state. Correlation with the structural features is fairly consistent with other similar data in the literature for one-dimensional copper (II) systems. Actually, the observed behaviour stems from a competition between the effect of the three ligands contributing to the exchange coupling between copper ions. Examining the literature on copper based magnetic systems shows that single or double End-On azido bridge can led to weak or strong antiferromagnetic coupling, or even ferromagnetic coupling depending of the geometry of the exchange pathway [13, 27, 28, 74]. The coupling through syn-syn carboxylate bridge is very versatile [23, 26] and the presence of DMSO can influence the whole magnetic interaction between neighbouring copper(II) ions [75]. These results enrich the data base available for further theoretical/experimental analysis of magneto-structural correlations in similar magnetic molecular systems. DFT calculations confirm that the copper ions are aligned ferromagnetically with an exchange coupling strength that compares very well with the experimental value. The robustness of exchange coupling with the variation of the distance and/or the angle between copper atoms indicates that the ferromagnetic order in the chain persists under external stimulus. Beyond magnetic features, copper based molecular systems are known to possibly exhibit bioassays and electronic cells applications [76-78], that could be envisioned in the near future for the present new copper-based coordination compound.

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Supplementary material:

Crystallographic data for **1** as CIF file (including structure factors) have been deposited at the Cambridge Crystallographic Data Centre as Supplementary publication N° CCDC 2032714. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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