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Azide, water and adipate as bridging ligands for Cu(II): Synthesis, structure and magnetism of $(\mu_4\text{-adipato-}\kappa\text{-O})(\mu\text{-aqua})(\mu\text{-azido-}\kappa\text{N}^1, \text{N}^1)$ copper(II) monohydrate

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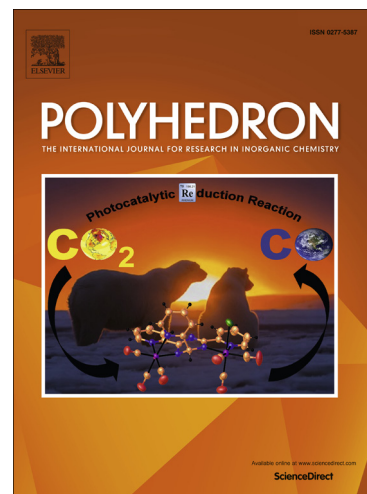
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Azide, water and adipate as bridging ligands for Cu(II): Synthesis, structure and magnetism of $(\mu_4\text{-adipato-}\kappa\text{-O})(\mu\text{-aqua})(\mu\text{-azido-}\kappa\text{N}^1, \text{N}^1)\text{copper(II) monohydrate}$

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Abstract:

The synthesis, characterization, single crystal structure and magnetic properties of the compound $[(\text{CuN}_3(\text{OH}_2))_2(\text{adp})]_n$ (**1**) are presented, in which adp stands for the adipate(2-) anion. This compound consists of layers containing chains of six-coordinated Cu(II) ions; the chains are connected by μ_4 -adipate anions. The magnetically interesting part of the compound is the Cu(II) chain, built from 3 bridging ligands, i.e. a water ligand, an azide anionic ligand bridging by using a terminal N atom to connect 2 Cu(II) ions, and one symmetrically bridging carboxylato group of adipate; the other end of the tetradentate adipate anions symmetrically connect the chains, forming the layers.

From the magnetic point of view the compound is considered as a Cu(II) chain with a quite unusual, symmetrical water bridge, the μ -syn-syn carboxylate and the $\mu\text{-N}_3$ bridge. The bridging water also hydrogen bonds to a terminal N of a nearby azido ligand. Magnetic susceptibility measurements show that **1** presents moderate ferromagnetic intrachain interactions ($J_{\text{chain}} = +38.4 \text{ cm}^{-1}$) with a metamagnetic behaviour for the inter-chain interaction with a critical field of 0.7 T.

Key words: copper; adipate; azide; ferromagnetic chain; metamagnet; water bridge

1. Introduction

Transition-metal coordination compounds with bridging ligands, like the rigid biscalboxylates are well known to form polynuclear structures (Coordination Polymers, or Metal organic frameworks). For compounds with the rigid terephthalic acid anions (benzene dicarboxylates) often very stable structures are formed [1-5]. With flexible biscalboxylates it is much more difficult to obtain rigid lattices, as observed in the adipate anion ($\text{OOC}-(\text{CH}_2)_4-\text{COO}^- = \text{adp}$), a ligand previously studied by us and others [6, 7]. Thus, only a small number of adipate complexes are recorded in the CSD and even less if we limit to Cu(II) complexes [8]. Some examples are $\{[\text{Cu}(\text{phen})_2]_2(\text{adp})\}(\text{ClO}_4)_2$, $\{[\text{Cu}_2(\text{phen})_2(\text{H}_2\text{O})]_2(\text{adp})_2\}(\text{ClO}_4)_4$ and $\{[\text{Cu}_2(\text{bpy})_2(\text{H}_2\text{O})]_2(\text{adp})_2\}(\text{ClO}_4)_4$ [9], $[\text{Cu}(\text{adp})(\text{imidazole})_4]$ [10] and a dinuclear melamine-adipate-bridged copper compound [11]. Our recent Cu and Ni compounds with the co-ligand bpy also belong to this category [6].

The adipate(2-) ligand is an easily accessible anion that can act as terminal or bridging ligand. As bridging ligand the most common coordination modes of the carboxylate groups are: chelating ($\kappa^2\text{O},\text{O}$), bridging with the two oxygen atoms: $\text{M}-\text{OCO}-\text{M}$ ($1\kappa\text{O};2\kappa\text{O}$) or with only one: $\text{M}-\text{O}-\text{M}$ ($1:2\kappa^2\text{O}$) and monodentate $\text{M}-\text{O}$ (κO).

We now have extended our previous studies by adding a bridging anion, i.e. the azide. Here we report our first results obtained with Cu(II): compound $[(\text{CuN}_3(\text{OH}_2))_2(\text{adp})]$ (**1**), where we observe an unprecedented Cu(II) chain with three different symmetric bridges, namely azido, water and carboxylato. Additional stabilization is obtained from a hydrogen bond of the bridging water molecule to a nearby terminal azido nitrogen. Full structural details as well as the magnetic properties of this metamagnetic chain are reported.

2. Experimental

2.1. Starting Materials

All the reagents and solvents used were purchased from commercial sources and used as received. All manipulations were performed in air.

2.2. Synthesis and crystal growth

The compound $[(\text{CuN}_3(\text{OH}_2))_2(\text{adp})]$ (**1**) was synthesized hydrothermally under autogenous pressure from a mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34 mg, 0.2 mmol), adipic acid (15 mg, 0.1 mmol) and NaN_3 (26 mg, 0.4 mmol) in water–methanol (4:1 v/v, 20 mL). The pH of the solution was adjusted to 6-7 with 0.2 M aqueous NaOH; then the mixture was sealed in a Teflon-lined autoclave and heated at 150 °C for 2 days and cooled to room temperature at a rate of 10 °C h⁻¹. The dark green

crystals of **1** were collected in ca 20% yield (based on Cu). Anal. calcd for **1**: C, 18.42; H, 3.09; N, 21.48%. Found: C, 18.27; H, 3.04; N, 21.82%. Main IR bands (ν , cm^{-1}): 3460 w, 2083 s [$\nu(\text{N}_3^-)$], 1534 s [$\nu_{\text{as}}(\text{COO})$], 1453 m, 1405 s [$\nu_{\text{s}}(\text{COO})$], 1287 m, 1132 m, 672 m.

CAUTION! Although not encountered in our experiments, azido compounds of metal ions are potentially explosive. Only a small amount of the material should be prepared, and it should be handled with care.

2.3. Physical and analytical characterizations

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. Infrared spectra were recorded using Thermo Scientific Nicolet iS10 in the range 3500-500 cm^{-1} . The electronic spectrum was performed in diffuse reflectance mode at room temperature in the range 200-1100 nm. The EPR spectrum was recorded at X band frequencies on crystalline powder at room temperature.

Magnetic susceptibility measurements were recorded on a Quantum Design MPMS-XL-5 SQUID magnetometer with different magnetic fields in the range 0.01-5.0 T in the temperature range 2-300 K. The isothermal magnetization was measured on the same sample at 2 K with magnetic fields up to 5 T. The susceptibility data were corrected for the sample holder (a sealed plastic bag) previously measured under the same conditions, and for the diamagnetic contributions as deduced by using Pascal's constant tables ($\chi_{\text{dia}} = -163.24 \times 10^{-6} \text{ emu.mol}^{-1}$) [12].

2.4. X-ray structure determination

A suitable dark blue-greenish crystal of the title compound was selected from its mother liquor and mounted on a glass fiber. Diffraction data were collected at 294 K using Mo $K\alpha$ radiations produced with a microfocus Incoatec μ sealed X-ray tube on a Kappa CCD (Bruker-Nonius) diffractometer equipped with an Apex2 CCD detector. The data collection was performed using APEX2 and SAINT [13] and the absorption correction using SADABS [13, 14]. The structure was solved using SHELXS-97 [15] and refined using SHELXL-2014 [16]. The H atoms bonded to C atoms were treated as riding atoms in geometrically idealised positions with C-H distances 0.97 Å; for the H atoms of the coordinated water molecule the atomic coordinates were refined giving O-H distances of 0.85(3) and 0.89(3) Å and an H-O-H angle of 107(3)°. The resulting difference map contained a large number of small but significant peaks, most plausibly assigned as partially occupied water sites, but no satisfactory model for these solvent molecules could be developed. Accordingly the SQUEEZE procedure [17] was applied at this stage. Relevant crystal and refinement data are listed in Table 1.

Table 1: Crystal and diffraction data with refinements for the title compound

Compound	1
Formula	C ₃ H ₆ CuN ₃ O ₃
Formula Weight	195.66
Crystal System	Monoclinic
Space group	C2/m
a (Å)	14.6420(14)
b (Å)	6.4964(6)
c (Å)	7.5403(7)
α (°)	90
β (°)	94.456(3)
γ (°)	90
V (Å ³)	715.07(12)
Z	4
crystal size (mm ³)	0.3x0.2x0.1
D _{calc} (g cm ⁻³)	1.817
Theta Min-Max (°)	3.74 < θ < 30.05
Dataset (h, k, l)	-20:20; -9:9; -10:9
F ₀₀₀	392
ρ _{min} , ρ _{max}	0.618, 0.739
Total reflections	10144
Unique reflections	2387
R _{int}	0.0099
R1 ^a	0.0196
wR ₂ ^b	0.0545
S ^c	1.096
parameters	62
restraints	0
data	1126

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for data with $F_2 > 2\sigma(F_2)$; ^b $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$ all data.

^c Goodness-of-fit $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

3. Results and Discussion

3.1. General observation

Despite several synthetic attempts varying the reagents ratio, only one compound could be obtained in a pure and reproducible form as crystals suitable for X-ray diffraction analysis. The compound has been characterized with C, H, N elemental analyses, IR spectra, EPR and electronic spectrum. Despite the different reagents ratio used, the stoichiometry of the final compound presents one adipate anion, two coordinated water molecules and two coordinated azide anions per two Cu(II) ions.

3.2. Structure of the Cu(II) compound

The compound [(CuN₃(OH₂)₂(adp)] (**1**) consists of Cu(II) ions, water molecules, azide ions and adipate (hexane-1,6-dioate) dianions in the ratio 2:2:2:1. The Cu ions lie on inversion centres (0.25, 0.25, 0.5) whereas the water molecules, the azide ions and the C atoms of the adipate

dianions all lie on mirror planes ($y = 0.5$). A projection of 2 units, showing the atom-numbering used and 2 chains is depicted in Figure 1. Pairs of Cu ions are linked by bridging water molecules, azide ions (coordinating at both Cu via the same terminal N atom) and one of the carboxylate groups of the adipate anion, thereby completing a CuN_2O_4 chromophore having the usual (4+2) coordination geometry with approximate C_{2h} symmetry in which the anionic ligands occupy the equatorial sites and the water molecules occupy the axial sites with much longer bond distances of 2.4825(12) Å due to the Jahn-Teller elongation, see Figure 2. The short equatorial distances are $\text{Cu-O}_{\text{adp}} = 1.9554(10)$ Å and $\text{Cu-N}_{\text{azide}} = 2.0064(9)$ Å. The overall geometry for each Cu is a Jahn-Teller elongated octahedron.

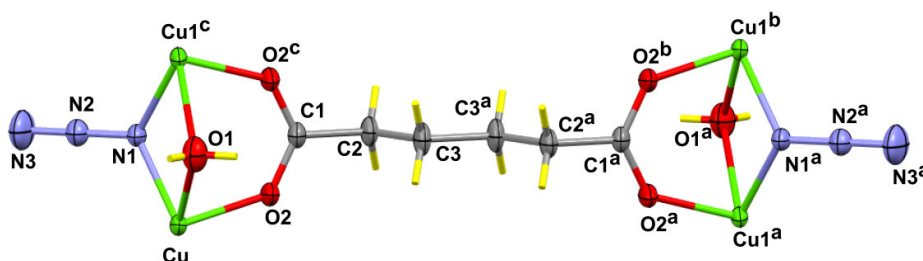


Figure 1. Two asymmetric units of compound **1** showing the atom-labelling scheme. Displacement ellipsoids for non-H atoms are drawn at the 50 % probability level, and H atoms are drawn as spheres of arbitrary radius. Symmetry operations: $a = 1-x, y, -z$; $b = 1-x, 1-y, -z$; $c = x, 1-y, z$. The Cu ions lie on centres of inversion and the water molecules lie on mirror planes, leading to the propagation of chains which run parallel to [010], i.e. the vertical direction in this diagram.

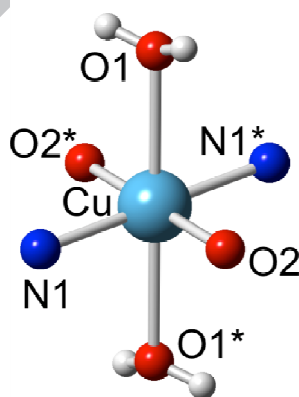


Figure 2. The coordination polyhedron around the centrosymmetric Cu ion (symmetry operation: $* = 0.5 - x, 0.5 - y, 1 - z$). The principal geometric parameters are $\text{Cu1-O1} = 2.4825(12)$ Å, $\text{Cu1-O2} = 1.9554(10)$ Å, $\text{Cu1-N1} = 2.0064(9)$ Å, $\text{O1-Cu1-O2} = 88.10(5)^\circ$, $\text{O1-Cu1-N1} = 80.93(4)^\circ$ and $\text{O2-Cu1-N1} = 90.40(5)^\circ$.

The symmetrically bridging water ligands are quite unusual, as well as the triple $\text{-COO}^-/\text{H}_2\text{O}/\text{N}_3^-$ bridge. In fact, a search in the CSD [8] (updated Feb 2016), shows only three complexes with such a triple bridge [18-20]. Interestingly, all of them are Cu(II) chains as the title compound,

but in these three cases the water bridge is asymmetric (the Cu-OH₂-Cu bond distances are: 2.564(5)/2.577(5) Å, 2.413(4)/2.504(4) Å and 2.376(3)/2.501(1) Å). Therefore, compound **1** is the fourth example of this kind of triple carboxylato/water/azido bridge and the first one in which the Cu-OH₂-Cu bridge has crystallographically imposed symmetry, as opposed to having two independent Cu-O distances of similar magnitude. Compound **1** is also the first one where the carboxylato bridge belongs to an alkyl chain (in the three other examples the carboxylato bridge is connected to an aromatic ring as 4-nitro-benzoato, 1-oxidopyridine-4-carboxylato and 6-hydroxynicotinato). This triple bridge gives rise to a very short metal-metal contact distance of 3.2482(3) Å, similar to those found in the other three examples with the same triple bridge (3.114(3), 3.120(9) and 3.2786(2) Å). The Cu-N and Cu-O_{adp} distances are in the normal ranges. However, the coordination geometry is quite distorted from octahedral. The plane with the 4 short Cu-L distances is significantly tilted with respect to the vertical axis (the angle between the apical O1-Cu-O1* axis and the average equatorial plane is 80.1°). Relevant bond lengths and angles around Cu can be seen in the caption of Figure 2.

Propagation of this coordination motif by inversion and reflection generates a chain running parallel to the [010] direction (Fig. 3). The adipate anion lies across an inversion centre at (0.5, 0.5, 0) and the [010] chains are linked into a two-dimensional coordination polymer in the form of a sheet parallel to (201) (see Fig. 3).

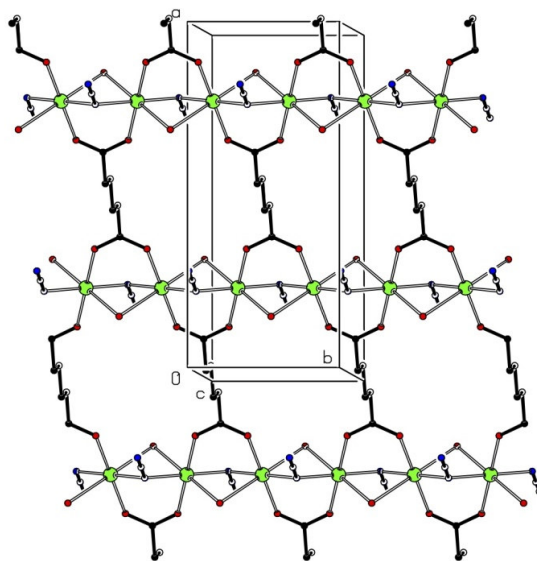


Figure 3. Crystal structure of compound **1** showing the Cu chains (along *b*) and a layer parallel to (102) plane.

The polymer sheets are themselves linked by O-H...N hydrogen bonds (Fig. 4), so forming a three-dimensional framework structure which encloses continuous channels running parallel to the [001] and [100] directions (see Fig. 5). Located within these channels are disordered, and possibly mobile, water molecules occupying multiple partially-occupied sites.

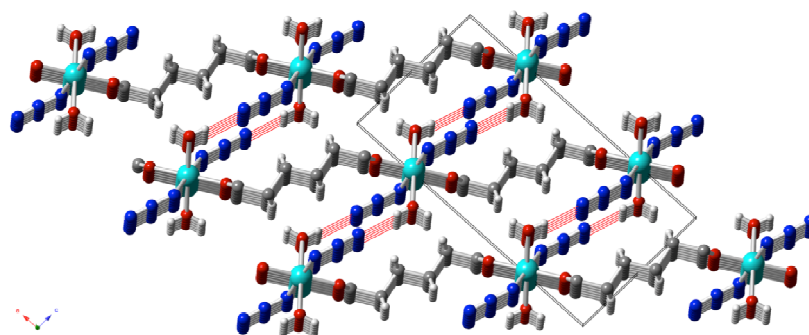


Figure 4. Crystal structure of compound **1** showing three layers parallel to the (102) plane. Red lines are the interlayer O-H...N hydrogen bonds.

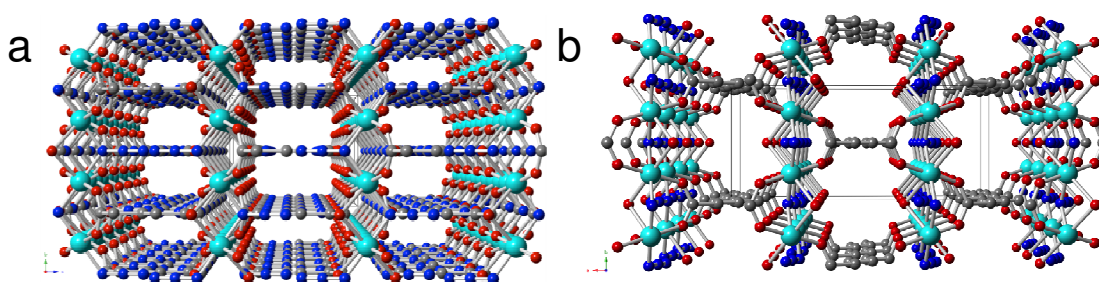


Figure 5. Perspective view of the channels formed in the structure of compound **1** (a) along the *a* axis and (b) along the *c* axis.

3.3. Spectroscopy and Magnetism

The IR spectrum shows the expected bands of adipate, water and azide. The strong azide stretching absorption at 2083 cm^{-1} is in the expected range for end-on bridging azides, i.e. $\mu_{1,1}\text{-N}_3$ coordination mode [21-23]. The solid state diffuse reflectance spectrum shows a broad band at 620 nm, typical for Cu(II) in a distorted octahedral geometry [24]. A band at 370 nm is assigned as a Ligand-to-metal (LM) charge transfer band. The powder EPR of compound **1** shows a single isotropic signal at $g = 2.16$ that may be attributed to the exchange narrowing of the Cu(II) ions along the chain. No signals for any dinuclear species are observed.

The product of the magnetic susceptibility per Cu(II) ion times the temperature ($\chi_m T$) for compound **1** shows at room temperature a value of ca. $0.5\text{ cm}^3\text{ K mol}^{-1}$, close to the expected one for a Cu(II) ion with $g \approx 2.3$ (Figure 6). On lowering the temperature, $\chi_m T$ shows a continuous increase, already observed at high temperatures, to reach a maximum at 14 K. The height of this maximum is $1.36\text{ cm}^3\text{ K mol}^{-1}$ when the applied field is 0.5 T (Figure 6 top) and $1.61\text{ cm}^3\text{ K mol}^{-1}$ for an applied magnetic field of 1 T (Figure 6 bottom). Below 14 K the $\chi_m T$ product shows a sharp decrease to reach a value of 0.25 or $0.35\text{ cm}^3\text{ K mol}^{-1}$ for applied fields of 0.5 or 1 T, respectively. This behaviour indicates that compound **1** presents a predominant moderate ferromagnetic intra-

chain Cu-Cu exchange coupling, responsible for the increase of $\chi_m T$ when the sample is cooled. The sharp decrease observed below the maximum may be due to an inter-chain antiferromagnetic interaction and/or to the zero field splitting of the ferromagnetic chain together with saturation effects at very low temperatures. Given the chain structure of compound **1**, we have used a simple $S = \frac{1}{2}$ regular ferromagnetic chain model to fit the magnetic properties of **1** [25]. This model reproduces very satisfactorily the magnetic properties of **1** above the maximum for an applied field of 0.5 T with $g = 2.222$ and $J_{\text{chain}} = +38.7 \text{ cm}^{-1}$ (red solid line in Figure 6a top). The Hamiltonian is written as $H = -J \sum S_i S_{i+1}$. Interestingly, this model is not able to reproduce the magnetic properties of compound **1** when they are measured with an applied magnetic field of 1 T (red solid line in Figure 6 lower panel).

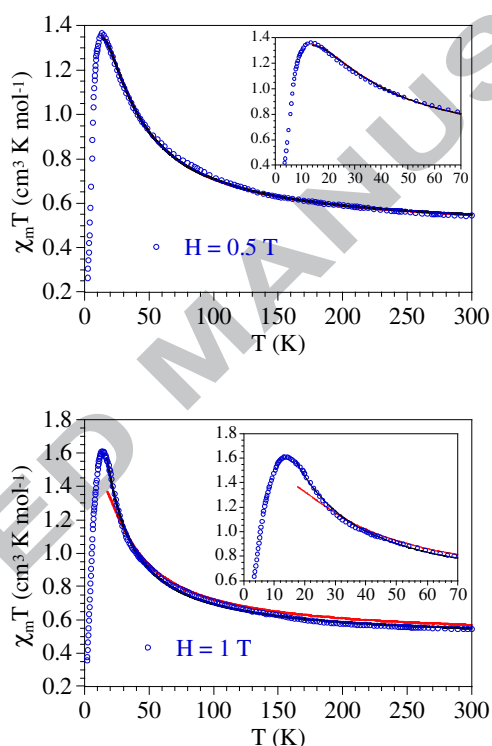


Figure 6. Thermal variation of $\chi_m T$ for compound **1** with an applied magnetic field of 0.5 T (**top**) and 1 T (**bottom**). Solid lines are the best fit to a simple regular ferromagnetic $S = \frac{1}{2}$ chain model without (red lines) or with (black lines) inter-chain interactions.

This result suggests that there must be an additional inter-chain interaction (j) which is mainly operative at high fields. Accordingly, we have fit the magnetic properties with the same $S = \frac{1}{2}$ ferromagnetic regular chain, but including an inter-chain interaction with the molecular field approximation [26]. This model reproduces much better the magnetic properties of **1** above the maximum for a magnetic field of 1 T with $g = 2.252$, $J_{\text{chain}} = +31.5 \text{ cm}^{-1}$ and $zj = +1.44 \text{ cm}^{-1}$ (z is the number of neighbours around each chain, black solid line in figure 6 lower panel). For the measurements with 0.5 T this second model including the inter-chain interactions reproduces also

very satisfactorily the magnetic properties of **1** above the maximum with $g = 2.227$, $J_{\text{chain}} = +38.4 \text{ cm}^{-1}$ and $z_j = -0.06 \text{ cm}^{-1}$ (black line in figure 6 top panel). Although the z_j value is very small at 0.5 T, this fit indicates that the inter-chain coupling is weakly antiferromagnetic for $H = 0.5 \text{ T}$ and weakly ferromagnetic of $H = 1 \text{ T}$. This behaviour suggests that **1** may be a metamagnet with a critical field in between 0.5 and 1 T.

Accordingly we have measured the isothermal magnetization of **1** at 2 K with magnetic fields up to 5 T (Figure 7). This measurement shows a slightly sigmoidal plot with a maximum slope of ca. 0.7 T (as deduced by the derivative of M vs. H , inset in Figure 7).

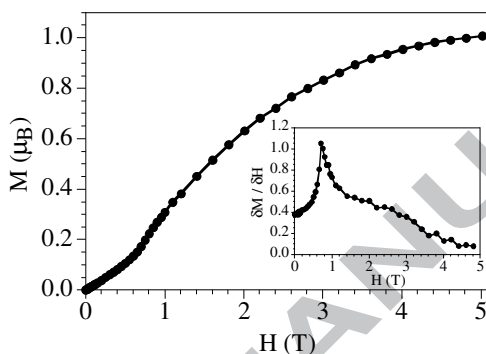


Figure 7. Isothermal magnetization of compound **1** at 2 K. Inset shows the derivative of M with H .

This metamagnetic behaviour implies that the interchain coupling in **1** is antiferromagnetic for low fields ($< 0.7 \text{ T}$), but ferromagnetic at high fields ($> 0.7 \text{ T}$), i.e., the inter-chain coupling is overcome by magnetic fields above 0.7 T. This assumption fully agrees with the behaviour observed in the thermal variation of $\chi_m T$ at 0.5 and 1 T and with the thermal variation of χ_m at different fields that shows a peak at ca. 8 K in χ_m only when the applied magnetic field is below 0.7 T (figure 8), suggesting the presence of an antiferromagnetic coupling for $H < 0.7 \text{ T}$.

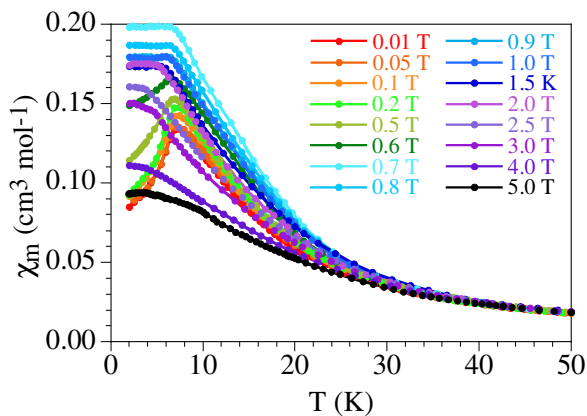


Figure 8. Thermal variation of χ_m for compound **1** with different applied magnetic fields in the range 0.01-5.0 T.

Interestingly, the other three known examples of Cu(II) chains with a triple $\text{COO}^-/\text{H}_2\text{O}/\text{N}_3^-$ bridge also show moderate-to-strong intra-chain ferromagnetic Cu-Cu couplings although only in one case the magnetic properties have been fitted. In this example the magnetic properties were fit to a ferromagnetic $S = 1/2$ regular chain model including an inter-chain interaction with the molecular field approximation with $g = 2.00$, $J = +97.85 \text{ cm}^{-1}$ and $z_j = -0.23 \text{ cm}^{-1}$ [20]. A second compound behaves as a metamagnet with strong ferromagnetic intra-chain interactions and weak antiferromagnetic inter-chain interactions and shows a spin-glass like behaviour [18]. The third compound also exhibits a strong intra-chain ferromagnetic Cu-Cu interaction [19].

In compound **1** the H_2O bridge is located on axial position in both Cu(II) ions and since the magnetic orbitals are the $d_{x^2-y^2}$ ones, we can assume that the magnetic coupling through the water bridge is negligible. In contrast, the symmetrical $\mu_{1,1}\text{-N}_3^-$ bridge with a Cu-N-Cu bond angle of $108.09(7)^\circ$ and a dihedral angle between the planes of the magnetic orbitals of 63.2° is expected to give rise to a strong antiferromagnetic coupling of ca. -150 cm^{-1} [27]. Additionally, the *syn-syn* carboxylato bridge is also expected to produce a moderate antiferromagnetic coupling [28]. Therefore, the ferromagnetic intra-chain Cu-Cu coupling found in compound **1** has to be explained with the counter-complementarity effect of the two antiferromagnetic couplings [29, 30].

Concluding Remarks

In summary, the compound $[(\text{CuN}_3(\text{OH}_2))_2(\text{adp})]$ (**1**) is a new regular Cu(II) chain compound with a unique triple symmetric azide/water/adipate bridge. The adipate anions connect neighbouring chains to form layers in the *ab* plane. These planes are further H-bonded to form an extended 3D H-bonded network. The magnetic properties show that the title compound is a metamagnet with moderate intra-chain ferromagnetic interactions ($J = +38.4 \text{ cm}^{-1}$) arising from the counter-complementarity effect of two antiferromagnetic bridges and a very weak antiferromagnetic interchain interaction that can be overcome with a critical magnetic field of 0.7 T.

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Supplementary information

The crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 1473802. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 (0)1223 336033 or Email: deposit@ccdc.cam.ac.uk.

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Azide, water and adipate as bridging ligands for Cu(II): Synthesis, structure and magnetism of $(\mu_4\text{-adipato-}\kappa\text{-O})(\mu\text{-aqua})(\mu\text{-azido-}\kappa\text{N}^1, \text{N}^1)\text{copper(II) monohydrate}$

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Text for graphs abstract:

The first compound with a triple symmetric water/azide/carboxylato bridge is a Cu(II) ferromagnetic chain with a metamagnetic behavior that has been structurally and magnetically characterized.

Graphics:

