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ARTICLE TYPE

Synthesis, crystal structure and magnetic properties of two alternating double $\mu_{1,1}$ and $\mu_{1,3}$ azido bridged Cu(II) and Ni(II) chains

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Two new alternating $\mu_{1,1}$ - and $\mu_{1,3}$ -azido bridged chains, $[\text{Cu}(\text{N}_3)_2(\text{mtn})]_n$ (**1**) and $[\text{Ni}(\text{N}_3)_2(\text{mtn})]_n$ (**2**) where mtn = N-methyl-1,3-propanediamine have been synthesized and characterized by single crystal X-ray diffraction. In both complexes, each metal atom is coordinated to six nitrogen atoms from four azide anions and one N-methyl-1,3-propanediamine molecule in a distorted octahedral geometry. In **1**, the basal-apical double $\mu_{1,1}$ -azido bridged Cu(II)-dimers are connected through two asymmetric $\mu_{1,3}$ -N₃ bridges to form a 1D chain in which one of the azide acts as a $\mu_{1,1,3}$ bridge while the other one is terminal. Structure of **2** is very similar but one of the azide ions acts as $\mu_{1,1}$ and the other as $\mu_{1,3}$ to form an alternating chain. Magnetic data of both compounds were fitted to an alternating ferro/antiferromagnetic chain model ($g = 2.120$, $J_F = +15.6 \text{ cm}^{-1}$, $J_{AF} = -2.6 \text{ cm}^{-1}$ and a paramagnetic impurity of ca. 0.4 % for **1** and $g = 2.180$, $J_F = +23 \text{ cm}^{-1}$ and $J_{AF} = -33 \text{ cm}^{-1}$ for **2**).

Introduction

Metal-azido complexes have attracted great research interest for many years due to their fascinating structural diversities, their importance in understanding magneto-structural correlations, and their promising potential applications as functional materials.¹ These studies have shown that the azido ligand has several different coordination modes, being the *end-on* ($\mu_{1,1}$) and *end-to-end* ($\mu_{1,3}$) the most abundant ones. It is also well established that the magnetic coupling strongly depends on the coordination mode of the azide ligand.¹⁻⁶ Thus, the $\mu_{1,1}$ bridging mode gives rise to ferromagnetic coupling, as far as the M-N-M angle is below ca. 104°, whereas the $\mu_{1,3}$ -N₃ bridges generates strong antiferromagnetic coupling.^{1,7} These abilities have been exploited to prepare azido-bridged compounds of Cu(II), Ni(II) and Mn(II) showing diverse magnetic properties as ferromagnetic⁸ and antiferromagnetic couplings,⁹ metamagnetism,¹⁰ spin canting,^{10,11} spin flop¹² and even single molecule magnets and single chain magnets.^{1b} Although the conditions leading to the $\mu_{1,1}$ and $\mu_{1,3}$ bridging modes are not well understood, a careful search in the CCDC data base shows that there are more than five hundred transition metal complexes with double $\mu_{1,1}$ -N₃ bridges and almost two hundred metal complexes with double $\mu_{1,3}$ -N₃. Interestingly, the formation of one or the other bridging modes seems to be quite exclusive in each particular system since there are only 18 structures presenting both types of double bridges in the same compound. Among these 18 structures, nine contain alternating double $\mu_{1,1}$ and $\mu_{1,3}$ bridges whereas the other nine contain 3D,¹³ 2D^{2c,3d} or different types of 1D structures with sequences formed by double $\mu_{1,1}$ and $\mu_{1,3}$ bridges (as $\mu_{1,1} + \mu_{1,1} + \mu_{1,3}$,¹⁴ $\mu_{1,1} + \mu_{1,3} + \mu_{1,3}$ ¹⁵ or even $\mu_{1,1} + \mu_{1,1} + \mu_{1,1} + \mu_{1,3}$ ¹⁶). Among the nine structures with alternating double $\mu_{1,1}$ and $\mu_{1,3}$

azido bridges, three contain Mn(II),^{15b,17} there are two with Cu(II),¹⁸ two with Ni(II),¹⁹ one with Co(II)^{18b} and one with Fe(II).^{18b}

Although in Ni(II) complexes the magneto-structural correlations through different azido bridges is well established, recently it has been found that azido-bridged Ni(II) compounds can present spin canting and slow relaxation.²⁰ It is well-known that spin canting arises from the presence of an antisymmetric exchange and the existence of single ion magnetic anisotropy. Various canted systems of Fe(II), Co(II), Ni(II) and Mn(III) ions which have large anisotropy have been characterized and magnetically investigated.²⁰⁻²²

Herein, we report the synthesis and magnetic properties of two very rare examples of chain compounds presenting alternating *end-on* ($\mu_{1,1}$) and *end-to-end* ($\mu_{1,3}$) azido bridges: $[\text{Cu}(\text{N}_3)_2(\text{mtn})]_n$ (**1**) and $[\text{Ni}(\text{N}_3)_2(\text{mtn})]_n$ (**2**) (where mtn = N-methyl-1,3-propanediamine). These compounds are formed by $\mu_{1,1}$ -N₃ and $\mu_{1,3}$ -N₃ bridges together with $\mu_{1,1,3}$ -N₃ (only in **1**). Both compounds show alternating ferro- and antiferromagnetic coupling which is attributed to the $\mu_{1,1}$ and $\mu_{1,3}$ azido bridges, respectively.

Experimental

Starting Materials

N-methyl-1,3-propanediamine was purchased from Lancaster and was of reagent grade. All the other reagents were of commercial sources and were used as received.

Caution! Azide salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Synthesis of $[\text{Cu}(\text{N}_3)_2(\text{mtn})]_n$ (**1**)

A clear solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (483.2 mg, 2 mmol) in methanol (5 mL) was mixed with the ligand N-methyl-1,3-propanediamine (mtn) (0.84 mL, 2 mmol) in methanol (10 mL) with constant stirring. After 10 min, 10 mL of a methanol-water solution (9:1, v/v) of NaN_3 (260.0 mg, 4 mmol) were added and the stirring was continued for another 15 min. The dark-green precipitate of complex **1**, which appeared immediately, was filtered and the filtrate was kept at room temperature. After 2-3 hours, single crystals suitable for X-ray diffraction analysis appeared at the bottom of the beaker.

Compound **1**: Yield: 326.0 mg. (69 %). Anal. Calc. for $\text{C}_4\text{H}_{12}\text{CuN}_8$ (235.77): C, 20.38; H, 5.13; N, 47.53 %. Found: C, 20.45; H, 5.08; N, 47.38 %. IR (KBr, cm^{-1}) bands: 3434, 3300, 3227, 2046, and 1383. UV-Vis spectrum, λ_{max} : 590 nm.

Synthesis of $[\text{Ni}(\text{mtn})(\text{N}_3)_2]_n$ (**2**)

Compound **2** was obtained by following a similar procedure to that of **1**, but nickel(II) nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (581.6 mg, 2 mmol) was used instead of copper nitrate trihydrate. Deep-green single crystals suitable for X-ray diffraction were obtained after 2 days. Phase purity of the bulk sample used for the magnetic measurements was checked by X-ray powder diffraction analysis (see Figure S1, supporting information).

Compound **2**: Yield: 310.0 mg. (67 %). Anal. Calc. For $\text{C}_4\text{H}_{12}\text{NiN}_8$ (230.89): C, 20.81; H, 5.24; N, 48.53 %. Found: C, 20.67; H, 5.08; N, 48.71 %. IR (KBr, cm^{-1}) bands: 3375, 3324, 3266, 2091, 2049, and 1293. UV-Vis spectrum, λ_{max} : 703 and 1015 nm.

Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4500-500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in the solid state (1400-250 nm) were recorded with a Hitachi U-3501 spectrophotometer. X-ray powder diffraction data were collected at room temperature in the 2θ range 5-40° on a Empyrean PANalytical powder diffractometer, using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$).

Magnetic measurements

Magnetic measurements were carried out on polycrystalline samples (with ca. 30.0 mg) with a Quantum Design MPMS-XL-5 SQUID susceptometer with an applied magnetic field of 0.1 T in the temperature range of 2-300 K. Isothermal magnetizations at 2 K were performed with magnetic fields in the range -5 to 5 T. The diamagnetic corrections were evaluated from Pascal's constants.

Crystallographic data collection and refinement

Suitable single crystals of each complex were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a

graphite monochromator and Mo-K_α ($\lambda = 0.71073 \text{ \AA}$) radiation. The crystals were positioned at 60 mm from the CCD. The structures were solved using Patterson method by using the SHELXS97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms that were refined with independent anisotropic displacement parameters. The hydrogen atoms bonded with carbon atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. The hydrogen atoms bonded to nitrogen atoms in **1** were located in a difference Fourier maps and refined without distance constraints. The hydrogen atoms bonded to nitrogen atoms in **2** were refined in calculated positions. Absorption corrections were carried out using the SADABS program.²³ All calculations were carried out using SHELXS 97,²⁴ PLATON 99,²⁵ ORTEP-32²⁶ and WinGX system Ver-1.64.²⁷ Data collection and structure refinement parameters and crystallographic data for the two complexes are given in Table 1. In (**2**), both N2 and C4 as disordered over two positions, i.e. A and B. The structure refined successfully with occupation factors of ca 0.50.

Table 1 Crystal data and structure refinement of complexes **1-2**

Complex	1	2
Formula	$\text{C}_4\text{H}_{12}\text{N}_8\text{Cu}$	$\text{C}_4\text{H}_{12}\text{N}_8\text{Ni}$
Mol. Wt.	235.77	230.89
Crystal System	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
a/Å	6.745(6)	6.879(2)
b/Å	7.383(7)	7.669(2)
c/Å	9.941(9)	10.216(3)
α (°)	103.341(10)	80.328(3)
β (°)	95.142(11)	88.967(3)
γ (°)	100.975(10)	64.213(3)
$V/\text{Å}^3$	468.2(7)	477.5(2)
Z	2	2
$D_c/\text{g cm}^{-3}$	1.672	1.610
μ/mm^{-1}	2.303	2.002
F(000)	242	240
R(int)	0.021	0.026
Total Reflections	3520	3615
Unique reflections	1988	2024
$I > 2\sigma(I)$	1523	1523
$R_1, wR_2(I > 2\sigma(I))$	0.0329, 0.0702	0.0407, 0.1034
T/K	293	293
GOF on F^2	1.111	1.020

Result and discussion

Description of structures

Complex 1

The single-crystal X-ray structural analysis shows that complex **1** is an azido bridged zigzag Cu(II) chain formulated as $[\text{Cu}(\text{N}_3)_2(\text{mtn})]_n$. The structure is formed by dinuclear neutral complexes, $[\text{Cu}_2(\text{N}_3)_4(\text{mtn})_2]$, resulting from the assembling of two mononuclear $\text{Cu}(\text{N}_3)_2(\text{mtn})$ units through two equivalent asymmetric $\mu_{1,1}\text{-N}_3$ bridges (Figure 1a). Selected bond distances and angles of compound **1** are listed in Table 2. The only independent copper atom, Cu1 is located in a distorted octahedral environment. The equatorial plane is formed by two nitrogen atoms, N1 and N2, from the chelating bidentate ligand N-methyl-1,3-propanediamine (mtn), a terminal azide nitrogen atom, N6 and a bridging azide nitrogen atom, N3. The four equatorial Cu-N bond lengths are in the range 2.004-2.046 Å (Table 2). The axial

positions are occupied by a nitrogen atom, N3' ($' = 2-x, 1-y, 2-z$) of a $\mu_{1,1}$ -N₃ bridge connecting Cu1 with its symmetry related

Cu1' atom and by a nitrogen atom, N5'' ($'' = 1-x, 1-y, 2-z$) of a

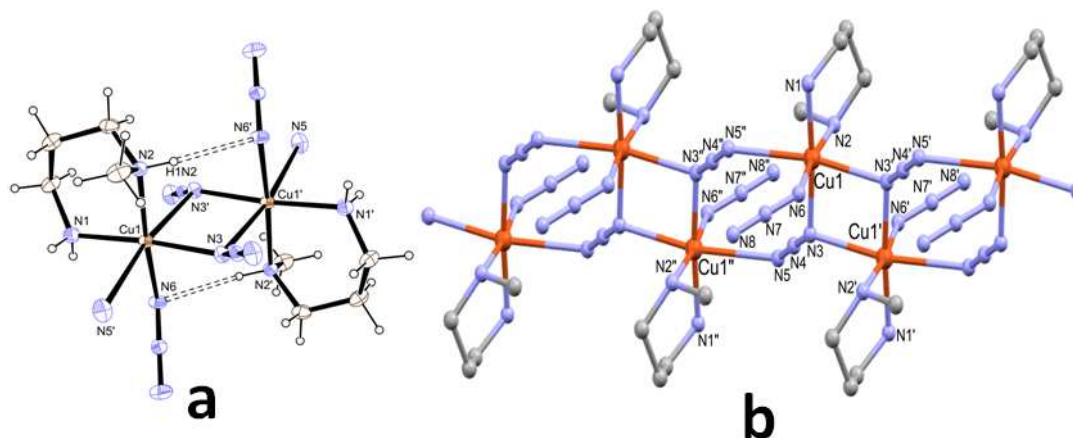


Fig. 1 (a) ORTEP view of complex **1**. Ellipsoids are drawn at the 30 % probability level. Symmetry transformation $' = 2-x, 1-y, 2-z$. Dashed lines are the intra-molecular H-bonds. (b) 1D polymeric chain of complex **1** along the crystallographic a axis. Symmetry transformation $' = 2-x, 1-y, 2-z$ and $'' = 1-x, 1-y, 2-z$. Hydrogen atoms have been omitted for clarity.

$\mu_{1,3}$ -N₃ bridge connecting this dimer with the neighboring one through a long Cu-N bond of 2.708(4) Å. Thus, the azide ligand N6-N7-N8 is terminal while the N3-N4-N5 one behaves as a $\mu_{1,1,3}$ -N₃ bridging ligand acting as an asymmetric $\mu_{1,1}$ -azide bridge through N3 to form the dimeric units [Cu₂(N₃)₄(mnt)₂] and, at the same time, acts as a $\mu_{1,3}$ -azide bridge (through N3 and N5) connecting neighboring dimers to form a zigzag chain with alternating double $\mu_{1,1}$ - and $\mu_{1,3}$ -azide bridges, as shown in Figure 1b. The deviations of the equatorially coordinated atoms from the mean plane passing through them are -0.110(4) Å for N1, 0.107(3) Å for N2, -0.111(3) Å for N3 and 0.114(3) Å for N6 and that of Cu1 from the same plane is -0.0245(4) Å directed towards the axial N5'' atom. The Cu1-N3-Cu1' bond angle is 95.53(11)°. The Cu1...Cu1' distance within the dinuclear unit through the double $\mu_{1,1}$ -azide bridge is 3.325 Å whereas the Cu1...Cu1' distance through the double $\mu_{1,3}$ -azide bridge is 6.745 Å.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex **1**

Atoms	Distance	Atoms	Angles
Cu(1)-N(1)	2.004(4)	N(1)-Cu(1)-N(2)	92.99(15)
Cu(1)-N(3)	2.014(4)	N(1)-Cu(1)-N(6)	88.10(15)
Cu(1)-N(2)	2.046(4)	N(2)-Cu(1)-N(3)	90.09(13)
Cu(1)-N(6)	2.028(4)	N(2)-Cu(1)-N(6)	172.36(14)
Cu(1)-N(5)''	2.708(4)	N(1)-Cu(1)-N(3)	174.36(14)
Cu(1)-N(3)'	2.458(4)	N(5)''-Cu(1)-N(6)	91.08(13)
		N(6)-Cu(1)-N(3)	89.47(13)
		N(3)-Cu(1)-N(3)'	84.47(11)
Atoms	Angles	Atoms	Angles
N(5)''-Cu(1)-N(3)'	171.34(11)	N(3)''-Cu(1)-N(2)	86.46(12)
N(3)''-Cu(1)-N(1)	100.42(14)	N(5)''-Cu(1)-N(3)	87.39(11)
N(3)''-Cu(1)-N(6)	85.90(12)	N(5)''-Cu(1)-N(2)	96.52(13)

25 Symmetry element $' = 2-x, 1-y, 2-z$ and $'' = 1-x, 1-y, 2-z$

The crystal packing of complex **1** shows that there are two types of hydrogen bonding interactions (Table 3): an intra-dimer one formed by the hydrogen atom H1N2 and the N6' atom of the terminal azide ligand and an inter-chain one involving the

30 hydrogen atom H1N1 and the N8''' atom ($''' = 1-x, -y, 2-z$) of a terminal azide ligand. This H-bond connects the chains to form a supramolecular layer (Figure S2).

Table 3 Hydrogen bonding interactions in complex **1**

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	\angle D-H...A (°)	Symmetry
N1-H1N1...N8	0.84	2.36	3.151(7)	156(5)	1-x,-y,2-z
N2-H1N2...N6	0.84	2.30	3.120(6)	164(3)	2-x,1-y,2-z

Complex 2

35 Compound **2** is also an azido bridged chain as **1** although in **2** the metal ion is Ni(II) and the coordination modes of the azido ligands are slightly different. As in **1**, two mononuclear [Ni(N₃)₂(mnt)] units are joined together through two equivalent $\mu_{1,1}$ -N₃ bridges to form dinuclear entities (Figure 2a) which are 40 linked each other through double $\mu_{1,3}$ -N₃ bridges forming a zigzag chain running along the a axis almost identical to the one observed in **1** (Figure 2b). The bond lengths and bond angles are summarized in Table 4.

Table 4 Selected bond lengths (Å) and bond angles (°) for complex **2**

Atoms	Distance	Atoms	Angles
Ni1-N1	2.066(3)	N3-Ni1-N2A	92.9(5)
Ni1-N2A	2.134(17)	N6-Ni1-N2A	104.0(4)
Ni1-N6	2.114(4)	N1-Ni1-N6	90.5(1)
Ni1-N3	2.138(4)	N1-Ni1-N6'	91.2(1)
Ni1-N6'	2.128(3)	N1-Ni1-N5''	88.5(1)
Ni1-N5''	2.110(4)	N3-Ni1-N6'	88.9(1)
Atoms	Angles	Atoms	Angles
N5''-Ni1-N6'	91.8(1)	N3-Ni1-N5''	91.9(1)
N5''-Ni1-N6	179.6(1)	N2A-Ni1-N6'	174.9(5)
N1-Ni1-N3	87.1(5)	N6-Ni1-N5''	172.5(1)
N1-Ni1-N2A	89.1(1)	N6-Ni1-N6'	80.8(1)
N3-Ni1-N6	89.1(1)	N2A-Ni1-N5''	83.4(5)

45 Symmetry element $' = 2-x, -y, 1-z$ and $'' = 1-x, -y, 1-z$

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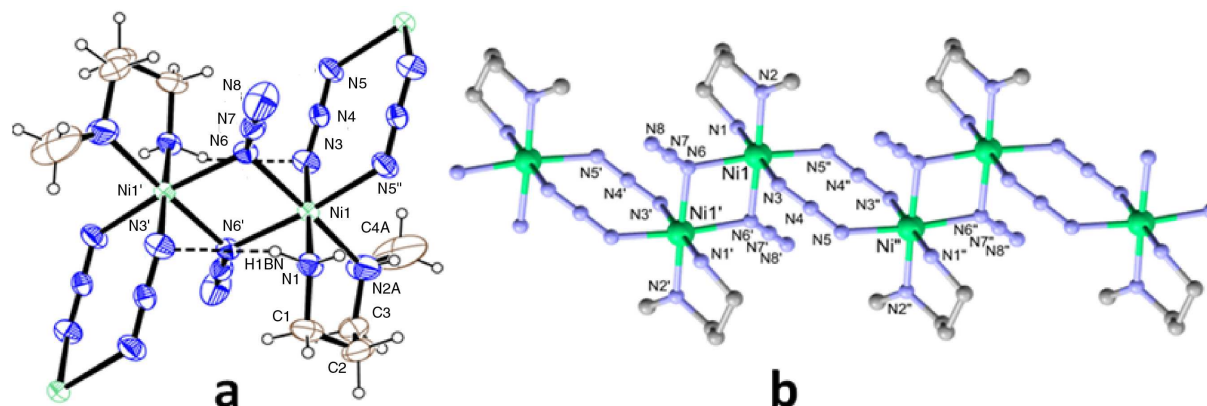


Fig. 2 (a) ORTEP view of complex **2**. Ellipsoids are drawn at the 30 % probability level. N2B and C4B atoms were omitted. Symmetry transformation $' = 2-x, -y, 1-z$. Dashed lines are the intra-molecular H bonds. (b) 1D polymeric chain of complex **2** along the crystallographic a axis. Symmetry transformation $' = 2-x, -y, 1-z$ and $'' = -1-x, -y, 1-z$. Hydrogen atoms have been omitted for clarity

The nickel(II) ion presents a slightly distorted octahedral NiN_6 environment formed by two nitrogen atoms, N1 and N2A, from a chelating bidentate N-methyl-1,3-propanediamine ligand (mnt) at 2.066(3) and 2.134(17) Å, two nitrogen atoms, N6 and N6' ($' = 2-x, -y, 1-z$) from two $\mu_{1,1}$ -N₃ bridges at 2.114(4) and 2.128(3) Å, and two nitrogen atoms, N3 and N5'' ($'' = 1-x, -y, 1-z$) from two $\mu_{1,3}$ -N₃ bridges at 2.138(4) and 2.110(4) Å, respectively. The octahedral geometry is close to regular, as shown by the six similar Ni-N bond lengths and the *cisoid* and *transoid* bond angles (in the range 80.8-104.0° and 172.5-179.6°, respectively).

The Ni1-N6-Ni1' bond angle through the $\mu_{1,1}$ -N₃ bridge (99.2(1)°) is within the normal range found in other similar Ni(II) complexes.^{1a,19b} The Ni1...Ni1 distances through the double $\mu_{1,1}$ -N₃ and $\mu_{1,3}$ -N₃ bridges are 3.229(1) and 5.138(2) Å, respectively. The crystal packing of complex **2** also shows the presence of two different types of hydrogen bonding interactions: (1) an intra-dimer one (as in **1**) formed by the amine hydrogen atom H1BN and the nitrogen atom, N3', of a $\mu_{1,1}$ -N₃ bridge (Table 5), (2) in contrast to **1**, in **2** the chains are connected through C-H...N hydrogen bonds formed between H2B of C(2) and the azide N(8)''' atom ($''' = -1+x, 1+y, z$). As in **1**, this H-bond connects the chains to form a layered structure (Figure S3).

Table 5 Hydrogen bonding interactions in complex **2**

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	$\angle\text{D-H...A}$ (°)	Symmetry
N1-H1BN...N3	0.90	2.50	3.223(5)	138	2-x, -y, 1-z
C2-H2B...N8	0.97	2.62	3.512(8)	153	-1+x, 1+y, z

It is to be noted that the main difference between the two structures (**1** and **2**) is that one of the azide is $\mu_{1,1,3}$ bridging and the other one is terminal in **1** while in **2**, one azide is $\mu_{1,1}$ and the other is $\mu_{1,3}$. Another noticeable difference is that in **1** the axial bonds are significantly longer than the equatorial ones due the Jahn-Teller distortion in Cu(II).

Magnetic properties of complex 1

The magnetic properties of complex **1** as $\chi_m T$ vs T plot (χ_m is the molar magnetic susceptibility per Cu^{II} ion) are shown in Figure 3 (and as χ_m vs. T in the inset). The value of $\chi_m T$ at 300 K is 0.38 $\text{cm}^3 \text{K mol}^{-1}$ which is the expected one for one magnetically quasi-isolated unpaired electron ($g \approx 2.00$). When the sample is cooled, $\chi_m T$ increases gradually up to 0.4 $\text{cm}^3 \text{K mol}^{-1}$ at 60 K and below 60 K they decrease quickly to reach a value of 0.04 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K. This behavior indicates the presence of ferro and antiferromagnetic exchange interactions. The isothermal magnetization at 2 K (Figure S4) corroborates a global antiferromagnetic coupling at low temperatures. The magnetization at 5 T is 0.3 μ_B , very far from the expected value for one isolated copper(II) ion (≈ 1.00 for $g \approx 2.00$). From the structural point of view, complex **1** is a one-dimensional polymer with alternating double $\mu_{1,1}$ and $\mu_{1,3}$ azido bridging ligands, even though one of the distances in the $\mu_{1,3}$ moiety is quite long, 2.708 Å. Since these azido bridges are well known to produce ferro and antiferromagnetic exchange interactions, respectively,^{7,28} we have fitted the susceptibility data to the model for an alternating $S = 1/2$ ferro/antiferromagnetic chain with the formula given by Borrás-Almenar et al.²⁹ The Hamiltonian is written as:

$$H = -\sum_{i=1}^{N-1} [J_{AF} S_{2i} S_{2i+1} + J_F S_{2i} S_{2i-1}] \quad (1)$$

where N is the number of spin pairs, J_F and J_{AF} are the nearest neighbors ferro- and antiferromagnetic exchange interactions. The best-fit parameters obtained are $g = 2.120$, $J_F = +15.6 \text{ cm}^{-1}$, $J_{AF} = -2.6 \text{ cm}^{-1}$ and a paramagnetic $S = 1/2$ impurity of ca. 0.4 % to account for the increase observed in the χ_m plot at very low temperatures.

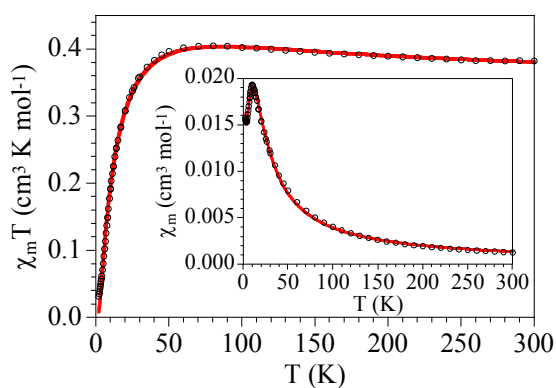


Fig. 3 Thermal variation of $\chi_m T$ for complex **1**. Solid line represents the best fit to the alternating ferro/antiferromagnetic $S = 1/2$ chain model (see text). Inset shows the thermal variation of χ_m .

The noticeable but not too strong ferromagnetic J_F value can be interpreted as a consequence of the existence of the two $\mu_{1,1}$ -azido bridges, which are expected to give rise to ferromagnetic coupling.⁷ Since these $\mu_{1,1}$ -N₃ bridges connect an equatorial position (2.014 Å) with an axial one (2.458 Å) the J value is expected not to be very strong. Furthermore, this weakening effect of the magnetic coupling should be more pronounced (but antiferromagnetic) in the $\mu_{1,3}$ -N₃ bridges since the axial Cu-N bond length is even longer (2.708 Å). Thus, it is not surprising that J_{AF} is only -2.6 cm^{-1} .

DFT calculations in these asymmetric azido-copper(II) bridges,⁷ show that the correlation between the calculated J value and the structural parameters (mainly the Cu-N₃-Cu angle) is not as straightforward as observed in symmetric azido bridges.²⁸ In these asymmetric bridges, connecting equatorial and axial positions (as in complex **1**), usually the coupling is small as the magnetic orbital describing the single electron is mainly of an x^2-y^2 type lying in the basal plane of the copper atoms and has only a small contribution on the axis perpendicular to the basal plane. From the magnetic point of view we can consider that the Cu(II) ions are penta-coordinated due to the long Cu1-N5 bond distance of 2.708 Å. The Addison parameter (τ) is very important in these cases.³⁰ In complex **1**, the Cu(II) ion has a τ value of 0.033. Considering, thus, distances, angles, and τ parameters the literature data corroborate the theoretical predictions, indicating a total dispersion of the J values with regard to these parameters.^{2,31-37}

Magnetic properties of complex **2**

The thermal variation of $\chi_m T$ per Ni(II) ion for complex **2** shows a room temperature value of ca. $1.2 \text{ cm}^3 \text{ K mol}^{-1}$, which is the expected value for one Ni(II) ion with $g \approx 2.2$ (figure 4). When the temperature is decreased $\chi_m T$ shows a continuous decrease to reach a value close to 0 at 2 K, suggesting the presence of predominant antiferromagnetic interactions in compound **2**. A further confirmation of these predominant antiferromagnetic interactions is also provided by the presence of a rounded maximum at ca. 25 K in the thermal variation of χ_m (inset in figure 4). As explained in the structural part, compound **2** can be considered as a one-dimensional complex with alternating double $\mu_{1,1}$ and $\mu_{1,3}$ azido bridges. According to the literature data, alternating antiferromagnetic and ferromagnetic magnetic interactions are expected for such a system.^{1a,19}

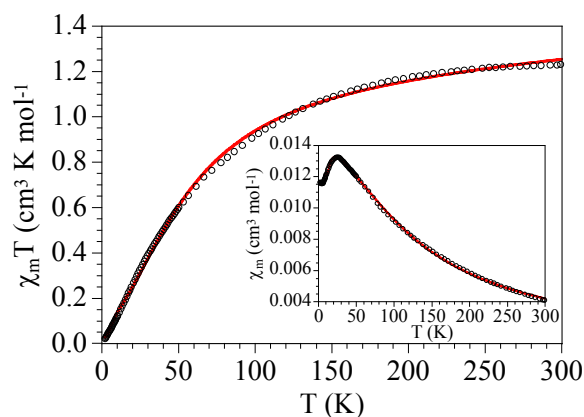


Fig. 4 Thermal variation of $\chi_m T$ for compound **2**. Inset shows the thermal variation of χ_m . Solid red line is the best fit to the alternating ferro/antiferromagnetic $S = 1$ chain model (see text).

To evaluate the intra-chain exchange parameters we have used the equation given by Borrás-Almenar et al. for this kind of alternating ferro/antiferromagnetic $S = 1$ chains.³⁸ The Hamiltonian is written as in (1). The fit of the experimental data (χ_m vs. T) with the above equation from 300 K to ca. 15 K gave as best parameters: $g = 2.180$, $J_F = +23 \text{ cm}^{-1}$ and $J_{AF} = -33 \text{ cm}^{-1}$, solid line in Figure 4). The results of the fit must be treated with caution, because we have taken only the experimental points above ca. 15 K and, accordingly, we have not included any zero field splitting of the $S = 1$ ions. As expected, the antiferromagnetic coupling constant (J_{AF}) is larger, in absolute value, than the ferromagnetic one and, accordingly, we have used the equation proposed for the case $0 < \alpha < 2.5$ ($\alpha = J_F/|J_{AF}|$).³⁸

The isothermal magnetization at 2 K (Figure S5, supporting information) confirm the antiferromagnetic coupling found in compound **2** and presents a very low saturation value of ca. $0.08 \mu_B$, arising from a small amount of paramagnetic impurities due to the presence of crystal defects and vacancies along the chain (the estimated amount is ca. 3.8 %).

Compound **2** presents a chain structure built up from dinuclear $[\text{Ni}_2(\mu_{1,1}\text{-N}_3)_2(\text{mntn})_2]$ units joined by double $\mu_{1,3}$ -N₃ bridges. Consequently, the magnetic behavior is the result of the behavior of two different interactions. In the $\mu_{1,1}$ -N₃ bridge, according to the literature data and theoretical calculations,^{1,28} the most important parameter determining the magnetic coupling is the Ni-N-Ni angle (θ). The interaction is predicted to be ferromagnetic for all the ranges of θ angles explored, with J increasing as the angle increases, yielding a maximum J value at $\theta \sim 104^\circ$. The only exception to this trend was found in the dinuclear bis($\mu_{1,1}$ -azido)nickel(II) complex reported by Chaudhuri *et al.*, due to an exceptionally small Ni-N-Ni angle.³⁹ In complex **2** the Ni-N-Ni angle is relatively small (99.17°) and, accordingly, the J value is ferromagnetic ($+23 \text{ cm}^{-1}$). Concerning the $\mu_{1,3}$ -N₃ bridge, the antiferromagnetic component of J is strongly dependent on the angle between the plane formed by the two $\mu_{1,3}$ -azido ligands and the N-Ni-N plane (in fact this is the main factor).^{1,40,41} The more planar the structure (dihedral angle close to 0°), the more antiferromagnetic is the coupling. In complex **2** this angle is 26.69° , explaining the relatively small J value (-33 cm^{-1}).

Conclusion

In summary, we report here two rare examples of similar alternating double $\mu_{1,1}$ -N₃ and $\mu_{1,3}$ -N₃ bridged Cu(II) and Ni(II) chains containing N-methyl-1,3-propanediamine as blocking ligand. Both chains present the expected alternating ferro-, antiferromagnetic exchange interactions attributed to the presence of alternating $\mu_{1,1}$ and $\mu_{1,3}$ azido bridges, respectively.

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Notes and references

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Graphical Abstract

Synthesis, crystal structure and magnetic properties of two alternating double $\mu_{1,1}$ and $\mu_{1,3}$ azido bridged Cu(II) and Ni(II) chains

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Two new alternating double $\mu_{1,1}$ and $\mu_{1,3}$ azido bridged 1D Cu(II) and Ni(II) complexes have been synthesized and their magnetic data were fitted to an alternating ferro/antiferromagnetic chain model.

