

Combining benzotriazoles and azides in copper(II) chemistry: synthesis, structural and spectroscopic characterization of a 1-D corrugated tape [Cu(N₃)₂(1-Mebta)]_n coordination polymer (1-Mebta = 1-methylbenzotriazole)

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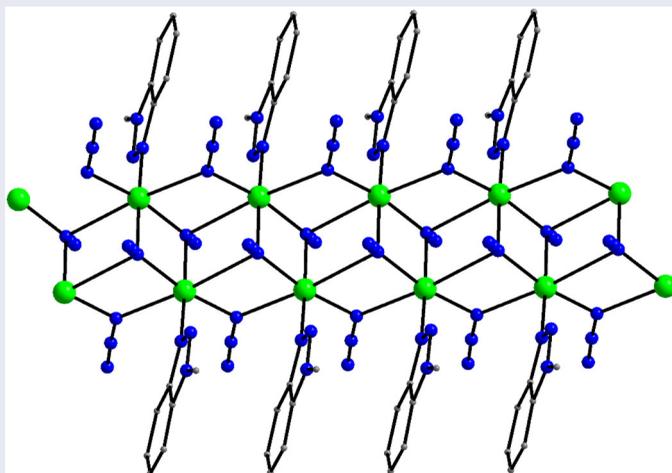
Combining benzotriazoles and azides in copper(II) chemistry: synthesis, structural and spectroscopic characterization of a 1-D corrugated tape $[\text{Cu}(\text{N}_3)_2(1\text{-Mebta})]_n$ coordination polymer (1-Mebta = 1-methylbenzotriazole)

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ABSTRACT

The tertiary $\text{Cu}^{\text{II}}/\text{N}_3^-/1\text{-Mebta}$ reaction scheme, where 1-Mebta is 1-methylbenzotriazole, led to the coordination complex $[\text{Cu}(\text{N}_3)_2(1\text{-Mebta})]_n$ (**1**), which has an unusual 1-D corrugated tape polymeric structure built by μ -1,1 and μ_3 -1,1,1 end-on bridging azido groups, and terminally bound 1-Mebta ligands. Solid-state IR and UV-Vis spectra of **1** are discussed in terms of its structure. The combined results demonstrate the flexibility of both the azido and 1-Mebta groups upon coordination with 3d-metal ions, and their usefulness in the synthesis of azido-rich Cu(II) coordination polymers.



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1. Introduction

Benzotriazole (btaH, [Figure 1](#)), and its derivatives [1], are well-known triatomic N',N'',N''' -based ligands in coordination chemistry and have contributed to the preparation of a plethora of structurally interesting compounds. These include: (i) polynuclear or polymeric compounds of 3d-metal ions, to model surface interactions and understand the role of benzotriazoles as corrosion inhibitors for metallic copper [2], (ii) large nuclearity coordination clusters with single-molecule magnet (SMM) behavior and large ground state spin values [3], and (iii) multidimensional coordination polymers with aesthetically pleasing structures and unusual luminescence and catalytic properties [4].

In contrast to btaH, the structurally similar 1-methylbenzotriazole (1-Mebta, [Figure 1](#)) is not an efficient corrosion inhibitor. Although 1-Mebta is potentially a bidentate N,N' -donor ligand, no coordination mode of 1-Mebta other than monodentate through $N-3$ has been reported for any coordination compound of any metal ion [5]. Thus, monodentate $N-3$ coordination can be regarded as the only coordination mode of 1-Mebta and other $N-1$ -substituted benzotriazoles containing groups with no donor atoms. This monodentate coordination is in part accountable for the absence of long-term corrosion inhibition on metals by 1-Mebta [6].

Our group has had a longstanding interest in coordination chemistry of 1-Mebta with Cu(II) [7], and many complexes have been reported by employing ancillary halides (i.e., Cl^- and Br^-) or anions with negligible binding capacity, such as ClO_4^- [8]. Murray and co-workers have also developed the chemistry of Cu(II) with 1-Mebta, and from the use of dicyanamide (dca^-) and tricyanamide (tcm^-) bridging ligands, they were able to isolate and characterize the 1-D coordination polymers $[\text{Cu}(\text{dca})_2(1\text{-Mebta})_2]_n$ and $[\text{Cu}(\text{tcm})_2(1\text{-Mebta})_2]_n$, respectively [9].

Azides (N_3^-) belong to the family of pseudohalides and constitute a class of versatile and multifunctional inorganic bridging ligands with applications in coordination clusters and polymers [10], organic synthesis [11], molecular magnetism [12], photochemistry [13], and high-energy materials [14]. From the coordination chemistry viewpoint, the azido group can link up to four metal ions when acting as a monoatomic N -bridge (end-on mode, EO) [15]. The coordination of both terminal N -donor atoms results in the end-to-end (EE) mode. The rare combination of both EO and EE modes is capable of bridging up to six metal ions [15]. The EO-bridging usually facilitates the formation of 0-D molecular clusters, while the EE mode is often found in polymeric (1-, 2- and 3-D) compounds [16].

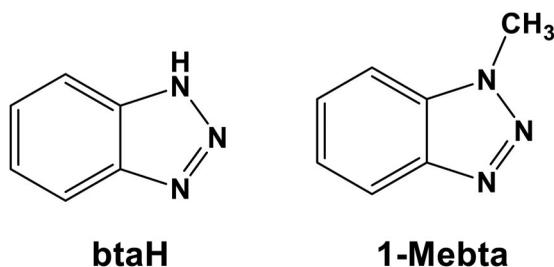


Figure 1. The organic ligands btaH (benzotriazole) and 1-Mebta (1-methylbenzotriazole) discussed in the present study.

The coordination chemistry of benzotriazole-based ligands has been recently reviewed [17]; a close look at this comprehensive report reveals the lack of structurally characterized $[\text{Cu}^{\text{II}}(\text{N}_3)_{2x}(\text{1-Mebta})_y]$ complexes. In this work, we report the synthesis, structural and spectroscopic characterization of a new 1-D coordination polymer with a corrugated tape motif that is built by coordination of Cu^{II} ions with end-on bridging azides and terminally bound 1-Mebta co-ligands. The reported $[\text{Cu}(\text{N}_3)_2(\text{1-Mebta})]_n$ (**1**) polymer enriches the continuously growing library of 3d-metal/benzotriazolate-type complexes, and it is the first azido-bridged compound of any metal that contains ancillary 1-Mebta ligands, thus presaging a new class of molecule-based species with interesting structures and potentially exciting physicochemical properties.

2. Experimental

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received, unless otherwise stated. Infrared (IR) spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded in the solid state using a Perkin-Elmer 16 PC spectrometer with samples prepared as KBr pellets. UV-Vis spectra were also recorded in the solid-state using a Hitachi U-2001 dual-beam spectrophotometer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 Series II Analyzer.

SAFETY NOTE: Azide and perchlorate salts, and their corresponding metal complexes, are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times. Complex **1** does not detonate on shock or spark under the reported synthetic conditions. The use of plastic spatulas is necessary for the safe isolation of the crystalline material.

2.1. $[\text{Cu}(\text{N}_3)_2(\text{1-Mebta})]_n$ (**1**)

To a stirred, green solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.07 g, 0.20 mmol) in DMF (10 mL) solids NaN_3 (0.03 g, 0.40 mmol) and 1-Mebta (0.11 g, 0.80 mmol) were gradually added. The resulting dark olive-green solution was stirred for 15 min, filtered, and the filtrate was left to slowly evaporate at room temperature. After 10 days, dark-green plate-like crystals of **1** were obtained and collected on a filter paper, washed with Et_2O ($2 \times 5\text{ mL}$), and dried in air. The yield was 35% (based on the total available copper). The air-dried microcrystalline solid was satisfactorily analyzed as **1**. $\text{C}_7\text{H}_7\text{CuN}_9$ (280.74): calcd. C 29.95, H 2.51, N 44.90%; found: C 30.07, H 2.63, N 44.82%.

2.2. Single-crystal X-ray diffraction data

A dark green-brown crystal of **1** was mounted in air and covered with epoxy glue. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation. Complete crystal data and parameters for data collection and refinement are listed in Table 1. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections from $13 < 2\theta < 23^\circ$. Intensity data were recorded using the θ - 2θ scan method. Three standard reflections monitored every 97 reflections showed less

Table 1. Crystal data and structure refinement for 1.

Empirical formula	C ₇ H ₇ CuN ₉
FW / g mol ⁻¹	280.76
Temperature / K	293(2)
Crystal type	Green-brown parallelepiped
Crystal size / mm ³	0.40 × 0.20 × 0.18
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	3.625(6)
<i>b</i> / Å	13.61(2)
<i>c</i> / Å	20.54(3)
α / °	90
β / °	91.06(5)
γ / °	90
Volume / Å ³	1013(3)
<i>Z</i>	4
ρ_{calc} / g cm ⁻³	1.841
μ / mm ⁻¹	2.148
F(000)	564
θ range / °	1.983 to 24.239
Radiation	Mo K α (λ = 0.71073)
Index ranges	0 ≤ <i>h</i> ≤ 4 -15 ≤ <i>k</i> ≤ 15 -23 ≤ <i>l</i> ≤ 23
Reflections collected	1629
Independent reflections	1367 (<i>R</i> _{int} = 0.0461)
Goodness-of-fit on <i>F</i> ²	1.121
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)] ^[a,b]	<i>R</i> ₁ = 0.0912 <i>wR</i> ₂ = 0.2882
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0997 <i>wR</i> ₂ = 0.2944
($\Delta\rho$) _{max,min} / e Å ⁻³	1.914 and -1.452

^[a] $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

^[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$ ($a = 0.1544$ and $b = 9.1811$).

than 3% variation and no decay. Lorentz, polarization and Ψ -scan absorption corrections were applied using the Crystal Logic software package. Given that the β -angle is close to 90°, the crystal presents pseudo-merohedral twinning with an additional 2-fold axis parallel to [001] direction, i.e., the twin law is (-1.0, 0.0, 0.0/0.0, -1.0, 0.0/0.21, 0.0, 1.0) and the refinement was performed with hklf5 data file with merged data (*R*_{int} = 0.0422 before merging) and the BASF parameter was refined to a value of 0.50(1). The structure was solved by direct methods and refined by full-matrix least-squares techniques on *F*² using SHELXL-2014/6 [18]. All hydrogens were introduced at calculated positions as riding on their parent atoms. All non-hydrogen atoms were refined anisotropically. Various figures of the structure were created using the Diamond 3 [19] and Mercury [20] software packages. The structure has been deposited with the CCDC as deposit number CCDC-2042236.

3. Results and discussion

3.1. Syntheses

The 1:2:4 reaction of Cu(ClO₄)₂·6H₂O, NaN₃ and 1-Mebta in DMF has led to a dark olive-green solution, from which dark green plate-like crystals of [Cu(N₃)₂(1-Mebta)]_{*n*} (**1**) were obtained in 35% yield. The same compound can also be formed by different

Cu(II) precursors, such as CuCl_2 , $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{O}_3\text{SCF}_3)_2$, albeit in much lower yields (5–15%). The 1:2:1 stoichiometric reaction of $\text{Cu}^{\text{II}}/\text{N}_3^-/1\text{-Mebta}$ in DFM has not yielded the expected complex **1** in higher yields, but instead the previously reported $[\text{Cu}_3(\text{N}_3)_6(\text{DMF})_2]_n$, which is organic ligand-free and has a 2-D polymeric structure built by end-on bridging azide ions [21]. It is likely that there is a competition between DMF and 1-Mebta for Cu^{II} binding sites. Probably, the reaction solution contains several species in equilibrium, with factors such as reaction ratios, concentrations, relative solubilities, lattice energies, crystallization kinetics and others determining the identity of the isolated products.

Reactivity studies were also performed as a means of altering the reaction mechanism, and eventually crystallizing and isolating new $\text{Cu}^{\text{II}}/\text{N}_3^-/1\text{-Mebta}$ products. First, the reaction solvent was proved not to be a 'key' parameter for preparation of new compounds but a crucial factor for the crystallinity of the resulting materials. In particular, several reactions of CuX_2 starting materials, NaN_3 and excess of 1-Mebta were performed in solvents such as MeCN, alcohols (MeOH, EtOH, etc), Me_2CO and MeNO_2 , and in all cases dark green solids were obtained, evaluated through IR spectroscopy and proved to be the same complex **1**. All crystalline forms of **1**, derived from different CuX_2 reagents, were obtained from combination of excess 1-Mebta and DMF as the reaction solvent. Lastly, the azido source was explored as a possible synthetic parameter for the chemical and structural manipulation of **1**. Alkali metal azides (i.e., LiN_3 and KN_3), akin to NaN_3 , had no effect on the chemical identity of **1**. However, when the organic azido precursor Me_3SiN_3 was employed in place of NaN_3 , dark olive-green crystals of the known, 1-Mebta free, 3-D coordination polymer $[\text{Cu}(\text{N}_3)_2]_n$ were obtained in good yields (40–55%) depending on the CuX_2 precursor [22]. We have recently shown that Me_3SiN_3 is a unique azido source for the synthesis of new 3d-metal/azido cluster compounds and multidimensional coordination polymers with unprecedented structural motifs and interesting magnetic properties, fostering the formation of crystalline molecular species without requiring the co-presence of any primary or ancillary organic chelates [23]. Unfortunately, in this case, the tertiary system $\text{Cu}^{\text{II}}/\text{Me}_3\text{SiN}_3/1\text{-Mebta}$ did not afford any new 1-Mebta-containing product, regardless the ratio of the three components and the reaction solvent. Our synthetic efforts and the corresponding results are summarized in Figure 2.

3.2. IR and UV-Vis spectroscopies

The IR spectrum (KBr pellets) of a dried sample of **1** (Figure 3) exhibits two very strong bands at 2098 and 2057 cm^{-1} , which are assigned to the asymmetric stretching mode, $\nu_{\text{as}}(\text{NNN})$, of the two types (2.20 and 3.30 using Harris notation) of end-on bridging azido groups with different degrees of asymmetry [24]. This is further evidenced by the appearance of $\nu_s(\text{NNN})$ vibrational modes in the range 1300–1270 cm^{-1} . For a symmetric N_3^- ion, the ν_s mode (ν_1) is IR inactive but Raman active, whereas $\nu_{\text{as}}(\text{NNN})$ (ν_3) and $\delta(\text{NNN})$ (ν_2) modes are IR active and Raman inactive [25]. The IR spectrum of free 1-Mebta exhibits bands at 1197 and 1110 cm^{-1} associated with the $\nu(\text{N}=\text{N})$ and $\nu(\text{N}-\text{N})$ modes of vibration, respectively [5, 7, 8]. These bands are shifted to 1228 and 1165 cm^{-1} , respectively, in the spectrum of **1**. These shifts are compatible with *N*-3

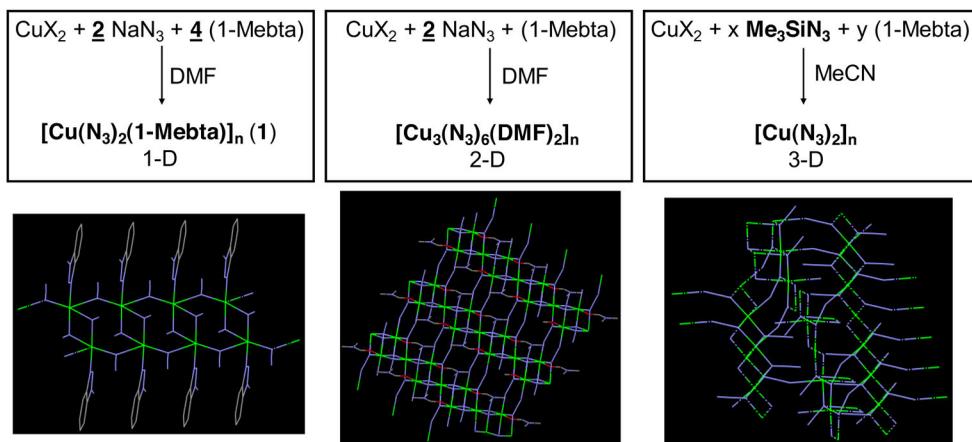


Figure 2. Schematic representation (and a representative wireframe drawing) of the synthetic routes followed for the preparation of **1** and the previously reported, organic ligand-free 2-D and 3-D polymers $[\text{Cu}_3(\text{N}_3)_6(\text{DMF})_2]_n$ and $[\text{Cu}(\text{N}_3)_2]_n$, respectively. Color scheme: Cu^{II} green; N blue; C grey.

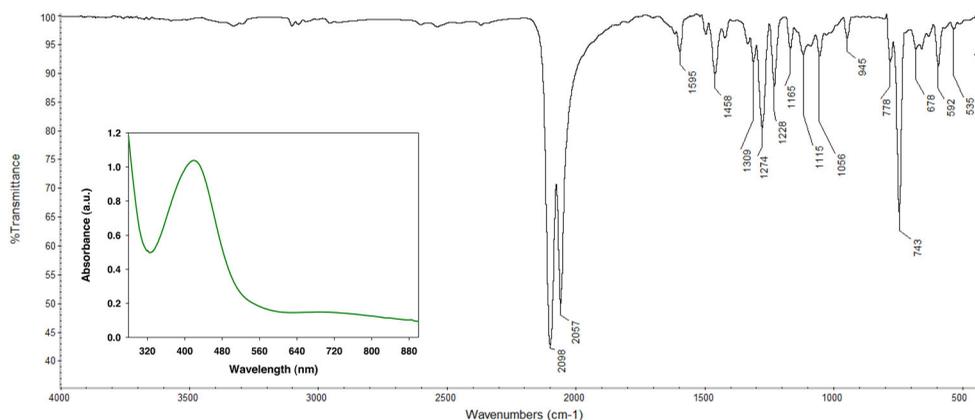


Figure 3. Solid-state IR and UV-Vis (inset) spectra of **1**.

being the donor atom to copper(II) [5, 7]. The coordinated 1-Mebta is considered responsible for the two bands at 778 and 743 cm⁻¹ in **1**; the latter is much stronger and assigned to the C-H out-of-plane vibration, while the former is due to a vibration involving both benzene and triazole in-plane bending [7c].

The UV-Vis spectrum of **1** was recorded in the solid-state due to solubility issues of the polymeric compound in organic solvents (Figure 3, inset). The absorption spectrum displays three major bands, all in agreement with the expected transitions of a distorted octahedral Cu^{II}N₆ chromophore [26]. The strongest band appears in the region of 200–300 nm (not shown in the inset of Figure 3), which is primarily due to intraligand transitions [27]. The band at 320–560 nm ($\lambda_{\text{max}} = 424 \text{ nm}$) can be assigned to ligand-to-metal charge transfer (LMCT), in accordance with previously reported compounds with similar nitrogen-to-copper charge-transfer transitions [28]. In addition to these bands, a weak but much broader band at 600–800 nm has been observed

Table 2. Selected interatomic distances (Å) and angles (°) for 1-3MeCN.^a

<i>Bond lengths</i>			
Cu-N21	1.972(10)	Cu-N11	2.019(8)
Cu-N3	1.988(9)	Cu-N11'	2.028(9)
Cu-N21'''	2.606(10)	Cu-N11''	2.824(10)
Cu...Cu'	3.104(4)	Cu...Cu'''	3.625(6)
Cu...Cu''	3.596(4)	Cu''...Cu'''	5.711(8)
<i>Bond angles</i>			
Cu-N11-Cu'	100.2(4)	N3-Cu-N11''	91.7(3)
Cu-N11'-Cu'	100.2(4)	N3-Cu-N11'	94.0(4)
Cu-N11-Cu''	94.5(3)	N3-Cu-N21'''	93.6(4)
Cu'-N11-Cu''	95.3(4)	N21-Cu-N11''	77.8(4)
Cu-N11'-Cu'''	95.3(4)	N11-Cu-N21	92.7(4)
Cu-N21'''-Cu'''	103.9(4)	N21-Cu-N21'''	103.9(4)
Cu-N11''-Cu''	94.5(3)	N11-Cu-N11''	85.6(3)
N3-Cu-N11	172.9(4)	N11-Cu-N11'	79.8(4)
N11'-Cu-N21	170.2(4)	N11-Cu-N21'''	89.0(4)
N11''-Cu-N21'''	174.4(3)	N11'-Cu-N11''	95.3(3)
N3-Cu-N21	93.1(4)	N11'-Cu-N21'''	82.4(4)

^aSymmetry codes: (') = -x, 1-y, -z; (') = 1-x, 1-y, -z; (''') = -1 + x, y, z.

($\lambda_{\max} = 687$ nm), which is ascribed to the d-d transitions from the metal ion in the distorted octahedral CuN₆ environment.

3.3. Crystal structure

Selected interatomic distances and angles of **1** are listed in Table 2. Compound **1** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains one Cu^{II} bound to two N₃⁻ ions and an 1-Mebta ligand. Expansion of the asymmetric unit reveals the overall 1-D corrugated tape motif of [Cu(N₃)₂(1-Mebta)] repeating units (Figure 4). Alternatively, the polymeric **1** can be described as two azido-linked, parallel 1-D linear chains which run along the crystallographic *c*-axis. The bridging between the Cu^{II} ions within each chain is achieved through two μ -1,1 (or 2.20) end-on bridging N₃⁻ groups (via N11 and N21 atoms); one of these N₃⁻ ligands (through N11 atom) becomes μ ₃-1,1,1 (or 3.30) end-on bridging and links the Cu^{II} ions of two neighboring chains resulting in the 1-D corrugated tape. Peripheral ligation about each Cu^{II} is provided by a terminally-bound (through N-3) 1-Mebta ligand. Each Cu^{II} center therefore possesses a N₆ chromophore, with (5 + 1) N-atoms originated from five coordinated N₃⁻ ions and one 1-Mebta ligand, respectively. The two crystallographically unique azide ions are almost linear with N-N-N angles of 177.4° (for the μ -1,1 N₃⁻) and 179.0° (for the μ ₃-1,1,1 N₃⁻), and they exhibit non-symmetric bond lengths (av. N-N distances of 1.15 and 1.20 Å).

The 1-Mebta ligands in **1** are intramolecularly stacked in an onset, parallel fashion; the centroid...centroid distance (yellow dashed lines in Figure 4) between adjacent, coordinated 1-Mebta groups is 3.625 Å. The Cu...Cu separations within each chain and between the neighboring, parallel chains are 3.625(6) Å and 3.104(4)/3.596(4) Å, respectively. The Cu-(μ -N₃⁻)-Cu angles in **1** span the range 94.5(3)-103.9(4)°.

The coordination sphere of Cu^{II} is highly elongated octahedral, as a consequence of the Jahn-Teller effect. The equatorial bond lengths are 1.972(10)-2.028(9) Å and the axial ones are 2.606(10) and 2.824(10) Å. According to Halcrow [29], an axial Cu-L (L = N/O/F donor atoms) distance of up to 2.4 Å might be considered as a genuine Cu-

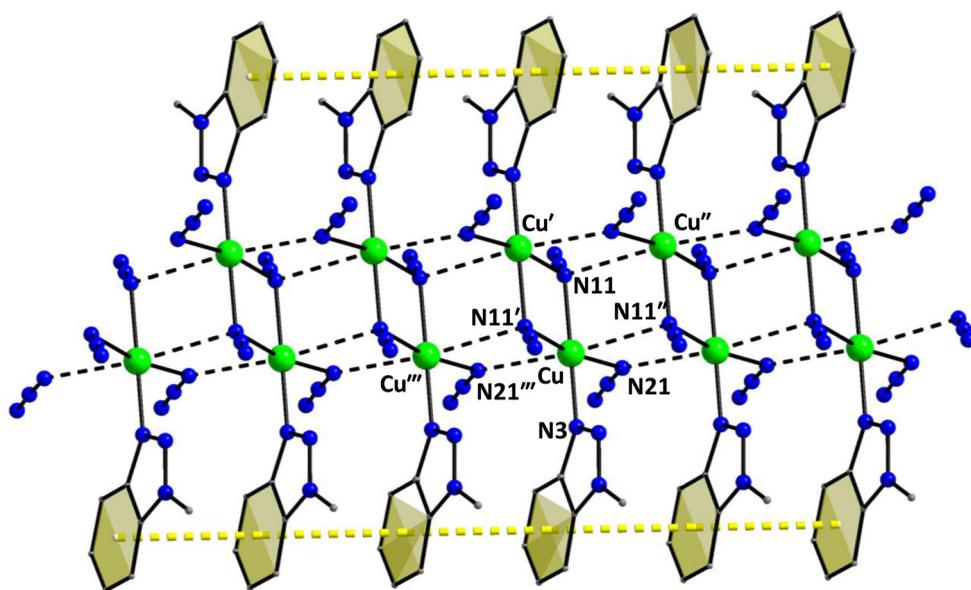


Figure 4. Partially labeled representation of a small section of the 1-D corrugated tape of **1**, comprising $[\text{Cu}(\text{N}_3)_2(1\text{-Mebta})]$ repeating units. The black dashed lines indicate the very long Cu-N distances, whereas the yellow dashed lines emphasize the intramolecular π - π stacking interactions between the phenyl rings of the coordinated 1-Mebta groups. Color scheme: Cu^{II} green; N blue; C grey. Hydrogens are omitted for clarity. Singly-, doubly-, and triply-primed atoms are related to the unprimed ones by the symmetry transformations: (') = $-x, 1-y, -z$; (')' = $1-x, 1-y, -z$; (''') = $-1+x, y, z$.

L bond, while a Cu-L distance within the range 2.4–2.8 Å better represents a weaker, secondary interaction, predominantly electrostatic in nature. To this end, the omission of the very long Cu-N11'' [2.824(10) Å] bond from the coordination sphere of the metal ions implies that a five-coordinate description may be equally valid. In this case, Cu^{II} ions in **1** should adopt an almost ideal square pyramidal geometry (trigonality index, $\tau = 0.03$, where τ is 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries [30], respectively), with the apical position being occupied by the N-atom of the other weakly-bound N_3^- ion [$\text{Cu-N21}''' = 2.606(10)$ Å].

Interestingly, the crystal packing of **1** (Figure 5) revealed the presence of very weak intermolecular interactions between adjacent double-chains. In particular, the phenyl rings of 1-Mebta ligands from neighboring corrugated tapes appear to be parallel displaced and weakly interacting through offset-type π - π stacking forces; the centroid...centroid separation is 5.869 Å and the angle between the ring normal and the centroid vector is 13.4° [31].

Qualitatively speaking and from a magnetic viewpoint, the Cu^{II} ions in **1** can be treated as a dimer (*i.e.*, of Cu and Cu') of doubly μ -1,1 (or 2.20) end-on azido bridging (through N11 and N11' atoms) because two of the $\text{Cu-N}_{\text{azide}}$ distances are very long (see Table 2). Density functional calculations on dinuclear complexes comprising the symmetrical $[\text{Cu}-(\mu_{1,1}\text{-N}_3)_2\text{Cu}]^{2+}$ core, reported by Ruiz et al., have shown that there is a clear correlation between the calculated J parameter and the θ angle, where θ is defined as the $\text{Cu-N}_{\text{azide}}\text{-Cu}$ angle [32]. The J value is expected to decrease from a

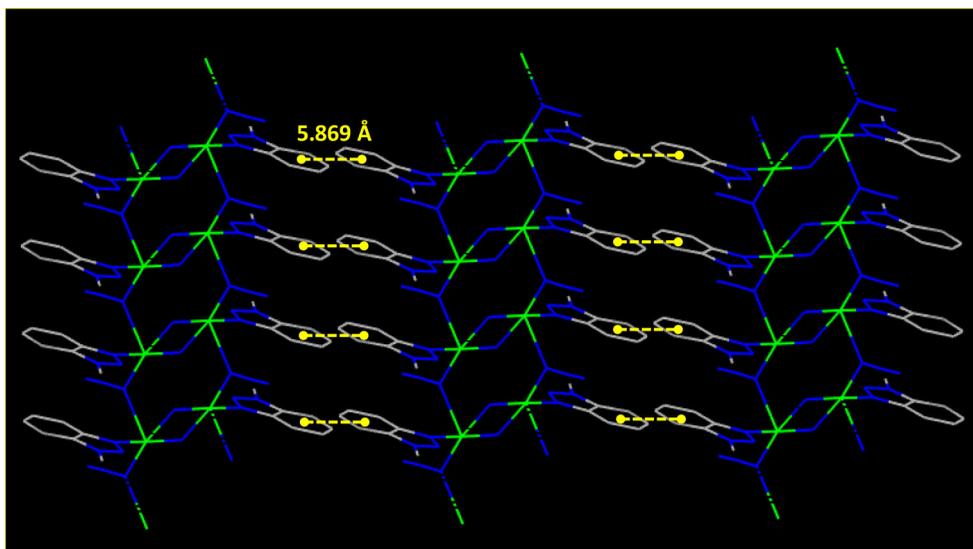


Figure 5. Supramolecular view of the packing of the 1-D double-chain pattern of **1**, highlighting with yellow dashed lines the inter-chain interactions between the phenyl rings of neighboring 1-Mebta groups. Color scheme as in Figure 4.

maximum at $\theta = 85^\circ$ upon increasing θ , corresponding to a ferromagnetic coupling, eventually reaching an antiferromagnetic regime for $\theta \geq 104^\circ$. The τ angle corresponding to the out-of-plane shift of the azide ligands should have negligible influence on the J value. In the case of the dinuclear magnetic core within **1**, the θ angle is $100.2(4)^\circ$ and the exchange interaction between the two Cu^{II} ions is expected to be ferromagnetic with a J value close to 100 cm^{-1} , according to the theoretical calculations and the magnetostructural criteria proposed by Ruiz and coworkers.

4. Conclusions and perspectives

We have herein reported the synthesis, crystal structure and spectroscopic characterization of a new 1-D coordination polymer of $\text{Cu}(\text{II})$ with an unusual corrugated tape structural motif, which is ensembled by end-on bridging azides and terminally coordinated 1-Mebta groups. The latter are arranged into a parallel, face-to-face conformation, thus providing additional thermodynamic stability to the compound through strong intra-chain π - π stacking interactions. Complex **1** is the first azido-bridged compound of any metal that contains 1-Mebta coordinated ligands and the first copper(II) azido complex with any benzotriazole ligand, and therefore our future research endeavors are oriented towards the development of this chemistry to other 3d- or 4f-metal ions with potentially exciting magnetic, optical and catalytic properties.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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