# An azido–Cu$^{\mathrm{II}}$–triazolate complex with utp-type topological network, showing spin-canted antiferromagnetism†

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**An azido–metal–1,2,4-triazolate coordination polymer, $[\mathrm{Cu(trz)(N_3)}]_n$ (trz = 1,2,4-triazolate) was synthesized using hydrothermal methods; the complex has a rare three-dimensional non-interpenetrated utp or (10,3)-d topological network structure and exhibits spin-canted antiferromagnetism at low temperature.**

In recent years, many researchers in the field of chemistry and materials science have been interested in the bulk magnetic properties of hybrid organic–inorganic materials.[1] Such materials are excellent candidates to study some of the fundamental magnetism phenomena, such as spin-canting, metamagnetism, *etc.*[2] One of the main challenges of this field is the design of molecular-based metal complexes exhibiting spontaneous magnetization. To achieve such magnetic entities a reasonable choice of bridging ligands is of ultimate importance because they can determine the magnetic strength and nature of the magnetic coupling between metal ions. Among the most widely used bridging ligands, azide is quite important, because it has many possible bridging modes that could lead to the formation of diverse structural topologies, and it is also easy to predict the magnetic nature of the coupling depending on its linkage modes and structural parameters,[3] sometimes, resulting in spin-canting, spin-flop and metamagnetism.[3c,d] However, in azido-metal systems, complementary organic ligands are always needed, to finely tune structures and magnetic properties. Indeed, until now the major emphasis in this field of research is the search for suitable organic co-ligands. On the other hand, 1,2,4-triazolate (trz) is also one such ligand, which can bridge metal ions to afford polynuclear or extended complexes and also has a superexchange capacity that is reflected in several unusual magnetic properties of its complexes.[4] On this basis, we speculate that combining both azide and trz anions in a metal complex might give some products with novel structures and interesting magnetic properties. Certainly, synthesizing complexes with azide and negative ligands is also a challenge due to the competitive coordination. However, a general solution reaction with nearly all transition-metal ions always gives precipitates. Recently, however, reports showed that the hydrothermal technique is effective to obtain crystal samples of metal–triazolate complexes.[4b,e] Thus, as a result of our attempts such a three-dimensional (3D) Cu$^{\mathrm{II}}$ complex, $[\mathrm{Cu(trz)(N_3)}]_n$ (**1**) was obtained by the hydrothermal reaction of 1,2,4-triazole (Htrz) with $\mathrm{CuCl_2}$ and $\mathrm{NaN_3}$ at 120 °C.‡ To the best of our knowledge, this is the first azido–metal coordination polymer with trz as co-ligand, although those with substituted trz have been documented.[3c] It should be pointed out that due to the potential explosive character of azide, hydrothermal synthesis is scarcely applied in the field. Thus, if the safety problem can be well handled, the hydrothermal method is promising in the synthesis of azido-metal complexes.

The phase purity of **1** was confirmed by XRPD (Fig. 1S, ESI†). The IR absorption at 2072 cm$^{-1}$ is attributed to the asymmetric stretching vibration of azide groups (Fig. 2S, ESI†). Single-crystal X-ray diffraction§ of **1** reveals that it crystallizes in the non-centrosymmetric space group *Pna*2$_1$. As shown in Fig. 1, each distorted square-pyramidal Cu$^{\mathrm{II}}$ center coordinates to three trz (Cu1–N 2.035(2) (N1), 2.028(2) (N3D) and 1.999(2) (N2C) Å) and one azide (Cu1–N4 1.988(2) Å) groups in the basal plane and to an apical azide ligand with an obviously elongated Cu–N bond (2.363(3) Å for N4C). The Cu$^{\mathrm{II}}$ center deviates from the mean equatorial plane by 0.1203(2) toward the apical site. Each trz links two Cu$^{\mathrm{II}}$ atoms in the *a* direction through the N1 and N2 donors and uses the third N donor to link to those in neighboring chains along *b* and *c* directions. The bridging angles of Cu1–N1–N2 and Cu1A–N2–N1 are 126.1(2) and 125.2(2)°, respectively, and the torsion angle of Cu1–N1–N2–Cu1A is 1.61(2)°, similar to those in relative complexes.[4a] As an additional bridge, azide bonds to two adjacent Cu$^{\mathrm{II}}$ in the chain in a single end-on (EO) mode (by occupying a bond in the basal plane of one Cu$^{\mathrm{II}}$ and the apical site of the other Cu$^{\mathrm{II}}$), with the angle of Cu1–N4–Cu1A being

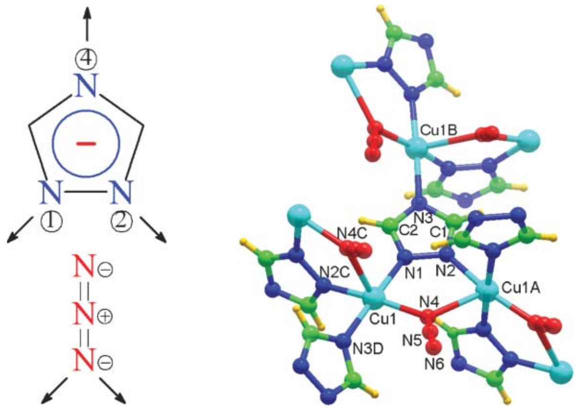

**Fig. 1** Left: scheme showing the linkages of trz and azide in **1**; right: local coordination environments (symmetry code A: 1/2 + *x*, 1/2 − *x*, *z*; B: 1/2 − *x*, 1/2 + *y*, *z* − 1/2; C: *x* − 1/2, 1/2 − *y*, *z*; D: 1/2 − *x*, *y* − 1/2, 1/2 + *z*).

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117.4(1)°. These bonding patterns produce an overall 3D framework containing a one-dimensional (1D) chain sub-structure (Fig. 2(a), (b)), in which the intra-chain Cu···Cu distance is 3.723(2) Å and inter-chain ones are 5.991(2) and 6.091(2) Å. Thus, the chain is constructed by a μ-1,2-bridging trz and EO-bridging azide ligands, being significantly responsible for the magnetic properties as discussed in detail later. In addition, the connectivity pattern produces several helical sub-structures along the crystallographic *b* and *c* directions as shown in Fig. 3S (ESI†). In the *c* direction, two types of helices are defined by both μ-1,2- and μ-1,4- (or μ-2,4-) for one and by only μ-1,4- (or μ-2,4-) trz groups for the other bridging $Cu^{II}$ atoms, with the number ratio of 1 : 2. In the *b* direction, there exists only one type of helix formed by alternatively μ-1,2- and μ-1,4- (or μ-2,4-) trz ligands bridging $Cu^{II}$ atoms. Neighboring helixes show opposite handedness.

Topologically, each trz ligand is connected to three adjacent $Cu^{II}$ atoms through three Cu–N bonds, and simultaneously each $Cu^{II}$ atom also links with three trz groups. Thus, each trz and $Cu^{II}$ atom can be defined as a three-connected node. As azide only acts as an additional bridging ligand, there is no need to consider it in the topological analysis. Based on this simplification, the structure of **1** can be described as a non-interpenetrated **utp**[5] (or (10,3)-d[6]) type topological network (Fig. 2(c), 4S, ESI†). The extended Schläfli symbol (vertex symbol) for this network is $10^2.10^4.10^4$. This is different from the regular **utp** net in three ways: (i) there exist two chemical types of nodes, and the edges and angles are not equivalent, (ii) the 4-fold screw axes in the regular **utp** net is lowered to 2-fold in the *c*-direction and (iii) the space group of **1** is $Pna2_1$, being lower than the *Pnna* for the most symmetrical configuration of the **utp** net. Comparing with **srs** and **ths**,[5] coordination polymers with the **utp** topological network are rare, especially for non-interpenetrated ones.[7]

It is interesting that **1** exhibits spin-canted antiferromagnetism at low temperature. The temperature dependence of the magnetic susceptibility was measured at 10 kOe in the range 2–300 K. The $\chi_M T$ *vs.* $T$ plot is shown in Fig. 3. The value of $\chi_M T$ per $Cu^{II}$ at 300 K is 0.359 $cm^3$ K $mol^{-1}$, slightly smaller than that expected for an isolated $Cu^{II}$ ion (0.375 $cm^3$ K $mol^{-1}$ and $S = 1/2$). On cooling, the $\chi_M T$ value decreases gradually until it reaches a minimum value of 0.06 $cm^3$ K $mol^{-1}$ at 30 K, which clearly indicates antiferromagnetic coupling between the $Cu^{II}$ ions in the lattice. It then increases to a maximum of 0.15 $cm^3$ K $mol^{-1}$ at 20 K and finally decreases again to 0.01 $cm^3$ K $mol^{-1}$ at 2 K, indicating a magnetic phase transition. To explain the magnetic interaction the possible exchange pathways need to be considered. The 3D framework of **1** consists of linear chains of $Cu^{II}$, in which each pair is bridged by an EO azide and a μ-1,2-trz ligand. The chains are arranged parallel in the 3D network and linked by the third N donor in trz. The main contributions for the magnetic exchange will be through the EO azide and μ-1,2-trz along the chain, with a weaker contribution of the inter-chain linkage. The data above 70 K can be modelled to a simple one-dimensional chain of $S = 1/2$ ions, to give $J = -46.8$ $cm^{-1}$ and $g = 2.14$ with a TIP of $6.0 \times 10^{-5}$ $cm^3$ $mol^{-1}$ per $Cu^{II}$ ion (Fig. 3).[8,9] Even though EO azide usually promotes ferromagnetic exchange, it can also lead to antiferromagnetic coupling as was calculated in complexes with Cu–N–Cu angles larger than 104°;[10] in fact, in **1** the Cu–N–Cu angle is 117°.

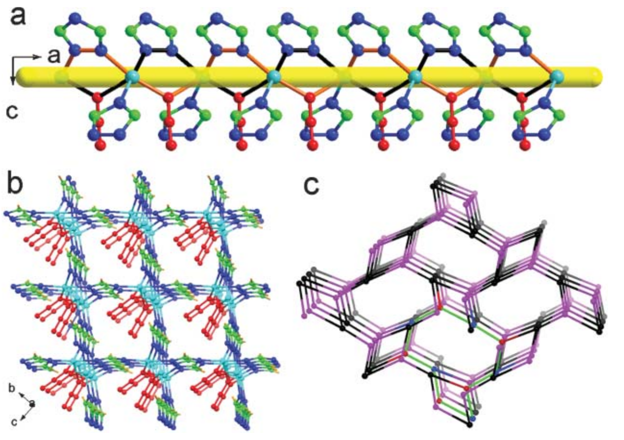

**Fig. 2** (a) 1D sub-structure of **1** showing a pair of opposite-hand helical linkages (orange and black bonds, H atoms omitted). (b) 3D structure of **1**, $Cu^{II}$ is shown as cyan, N as blue, C as green, H as orange and azide as red. (c) Schematic representation of the **utp**-type topological network with trz being represented by purple and $Cu^{II}$ by black spheres (a ten-membered ring is highlighted in green).

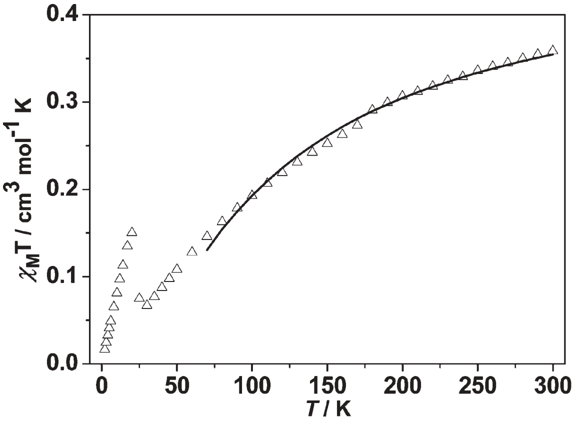

**Fig. 3** Temperature dependence of $\chi_M T$ for **1**. The line across the $\chi_M T$ curve represents the best fit to a one-dimensional chain of $S = 1/2$.

The increase in $\chi_M T$ observed at low temperatures corresponds to the onset of a very weak ferromagnetic state due to spin canting of the antiferromagnetically coupled $Cu^{II}$ ions. Furthermore, the susceptibility below 30 K is field dependent, as shown in Fig. 4(a), consistent with spin canting. The decrease in $\chi_M T$ below 17 K results from the saturation at high magnetic field and possible antiferromagnetic interchain interactions. This is verified by comparing the field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities (Fig. 4(b)). The divergence observed in FC and ZFC indicates the history dependence of the magnetization process. The field dependence of the magnetization, $M(H)$ at 2 K (Fig. 4(c)) shows an abrupt increase of the magnetization at fields below 10 Oe and a steady increase above that to 0.028 at 50 Oe, without achieving saturation. The hysteresis loops measured at 2 K are consistent with a very weak ferromagnetism (Fig. 4(c) inset), the coercive field is *ca.* 200 Oe, being characteristic of a soft magnet and the remnant magnetization is 0.0028. The spontaneous magnetization observed is due to spin canting, with an estimated canting angle of 0.16° ($\psi = \tan^{-1}(M_r/M_s)$).[11] It is well-known that the occurrence of spin canting usually is caused by either single-ion

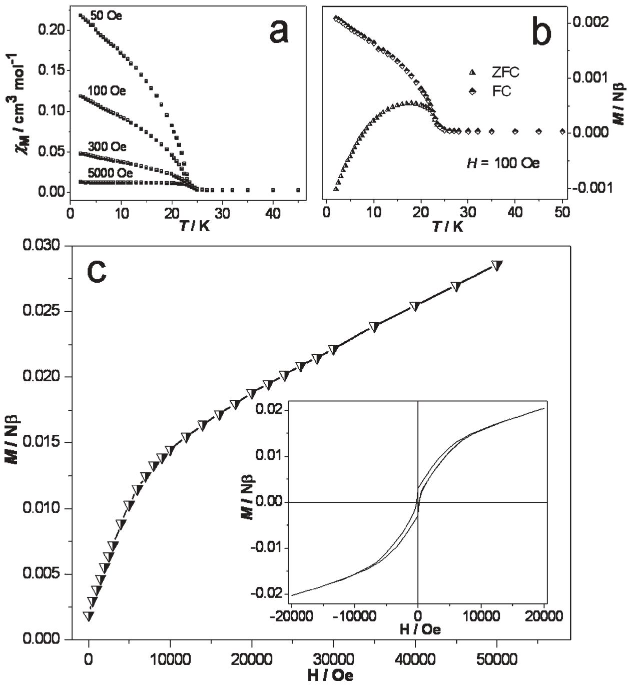

**Fig. 4** (a) Temperature dependence of $\chi_M$ at different fields of **1**. (b) The zero-field-cooled (ZFC) and field-cooled (FC) magnetization. (c) Field dependence of magnetization and hysteresis loop (inset) at 2 K.

magnetic anisotropy or antisymmetric exchange in magnetic entities.[2] In **1**, the observed spin canting may be attributed to the antisymmetric magnetic exchange, which is related to the symmetry of the magnetic entities. Actually, the axes defined by the apical bond around each Cu$^{II}$ are not parallel along the polymeric chain, which means that they are tilted with respect to each other. The Cu$^{II}$ positions are also not related by an inversion centre, and thus, because they are tilted the spins do not completely cancel. Of course, the 3D superexchange in the acentric structure of **1** may also need to be considered. Although canted antiferromagnetism has been found in some metal coordination complexes, it is not common for Cu$^{II}$ systems, except for some recently reported examples.[12]

In summary, the first azido–metal–triazolate coordination polymer was synthesized by a hydrothermal method. This complex displays a rare 3D **utp**-type network structure and shows spin-canted antiferromagnetism at low temperature, further demonstrating the potential of azido and triazolate ligands in constructing magnetic coordination polymers. The possible extension of this work to other metals is in progress, with special interest in the Co$^{II}$, Ni$^{II}$ and Mn$^{II}$ derivatives.

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## Notes and references

‡ *Synthesis* of $[Cu(trz)(N_3)]_n$: A mixture of 1,2,4-triazole (Htrz, 35 mg, 0.5 mmol), $NaN_3$ (98 mg, 1.5 mmol) and $CuCl_2{\cdot}2H_2O$ (136 mg, 0.8 mmol) in 10 mL of $H_2O$ was sealed in a Teflon-lined autoclave (23 mL) and heated at 120 °C for 48 h, and then allowed to spontaneously cool to room temperature. Black–green crystals were collected and washed sequentially by water and acetone. Yield: ~50% based on Htrz. Analysis (%): Calc. for $C_2H_2CuN_6$: C 13.84, H 1.16, N 48.40. Found: C 13.76, H 1.02, N 48.84. IR spectrum, see ESI.† ***CAUTION***! Although we have encountered no problems in handling Cu-azido during this work, it should be treated with great caution owing to their potential explosive nature. Thus, it should only be handled in small amounts. In our experiment, the dosage of $NaN_3$ and $CuCl_2{\cdot}2H_2O$ did not exceed 100 and 150 mg, respectively, and the used $H_2O$ does not go beyond 15 mL in the 23 mL autoclave.

§ *Crystal data* for **1**: $C_2H_2CuN_6$, $M_r$ = 173.64; orthorhombic; $Pna2_1$; $a$ = 6.7054(13), $b$ = 9.0818(18), $c$ = 8.1187(16) Å, $V$ = 494.41(17) Å$^3$; $Z$ = 4; $D_c$ = 2.333 g cm$^{-3}$; $T$ = 293(2) K; collected/unique = 4548/1128; $R_{int}$ = 0.0412; $R_1$ = 0.0234, $wR_2$ = 0.0537 ($I > 2\sigma(I)$); $R_1$ = 0.0266, $wR_2$ = 0.0560 (all data) and GOF = 1.042; Flack parameter = 0.02(3). The terminal N atom of $N_3^-$ is disordered, and was refined in two sites with a 1 : 1 occupancy. CCDC 635768. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702988h

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