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Tetrazolate-azido-copper(II) coordination polymers: tuned synthesis, structure, and magnetic properties†

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Abstract

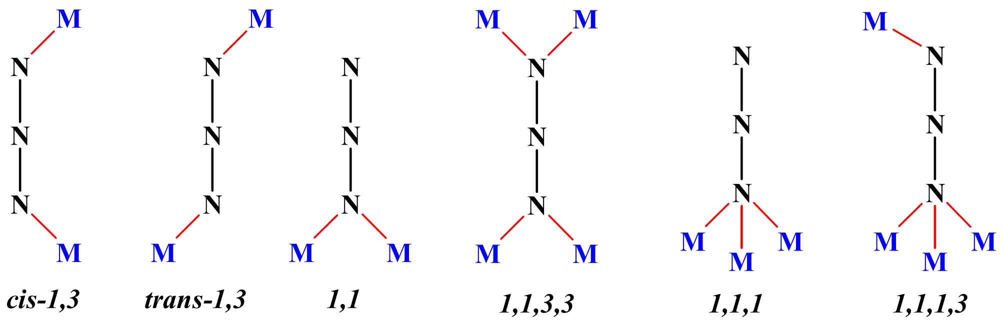
As the first example of using parent tetrazole and azide together in preparing magnetic complexes, two novel tetrazolate-azido-bridged Cu(II) coordination polymers, $[Cu(tz)(N_3)]_n$ (**1**) and $[Cu(tz)(N_3)(NH_3)_2]_n$ (**2**) (tz = tetrazolate) have been synthesized through the reaction of Htz, $CuCl_2$, and NaN_3 under hydrothermal condition and in the ammonia solution at room temperature, respectively. The single crystal X-ray structure analysis reveals that the two complexes possess distinct three-dimensional (3D) framework structures and can be topologically described as a 3-connected *srs* ($SrSi_2$) type net and a 4-connected *cds* ($CdSO_4$) type net, respectively. Both tetrazolate and azide groups also have different linkage modes in the two complexes. **1** contains end-on (EO) type azide bridge and 3-connected tetrazolate, while **2** possesses end-to-end (EE) azide linker and 2-coordinated tetrazolate. Magnetic measurements indicate that antiferrimagnetic interactions are dominated between the Cu(II) ions in the two complexes, with corresponding magnetic coupling being $J = -41.0\ cm^{-1}$ in **1** and $J = -8.62\ cm^{-1}$ in **2**.

Introduction

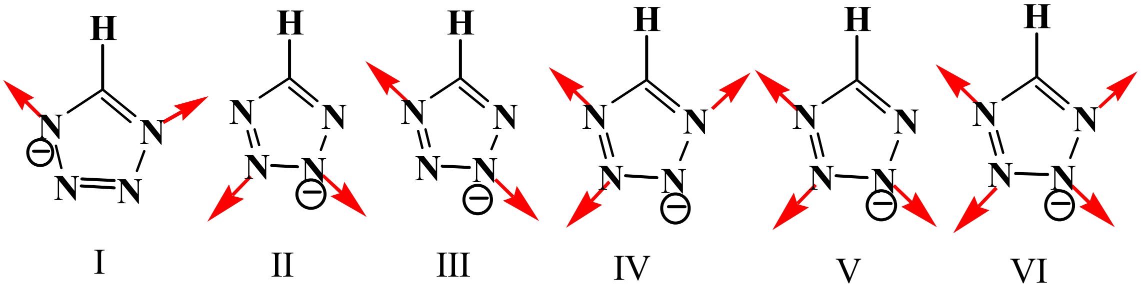
Investigation into the structural and magnetic properties of transition metal complexes has become a fascinating subject in the field of coordination chemistry.[1] The common synthetic approach of molecular magnetic materials is to incorporate paramagnetic centers with suitable bridging ligands to fabricate complexes that can give rise to magnetic exchange coupling. Besides the metal centers, the nature and the linking modes of the bridging ligand also play crucial roles in tuning the whole magnetic properties of resulting complexes. Therefore, the search and exploration of appropriate bridging ligands is a long standing task in this field.

As a pseudohalide anion, the linear azide ion, having a rich variety of coordination modes (Scheme 1) and being good mediators for transmitting magnetic coupling between paramagnetic metal centers because of their short lengths, has been widely utilized as bridging ligands in the construction of magnetic materials with interesting structural and magnetic features.[1a,2] When acting as bridging ligand, there are two typical coordination modes for the azide ion: end-to-end (EE or 1,3) and end-on (EO or 1,1) mode. Normally, the end-to-end (EE) coordination mode gives antiferromagnetic coupling while the end-on (EO) transfers ferromagnetic coupling.[3] Despite the richness of the metal-azide structural chemistry, only a few three-dimensional (3D) coordination networks[1a,4] are reported among large numbers of azide compounds found in the Cambridge Structural Database.[1a,5] Therefore, the previous investigations of metal-azido systems had been mainly focused on the low dimensionalities. However, high-dimensional networks of metal-azido derivatives are of particular interest because of their novel topology and the enhancement of bulk magnetic properties, as well as their magnetostructural correlations.[6]

The common strategy employed for the synthesis of a high-dimensional metal-azido system is the further extension of metal-azido assemblies by using additional organic linkers.[7] Up to date, a large number of complementary organic ligands have been employed in this regard.[7] Among them, five-membered heterocyclic azoles (triazoles, tetrazoles, etc.) and their derivatives are drawing much attention due to their strong σ-electron donors to metals, diverse coordination modes, and strong super-exchange capacity.[8] As multi-functional bridging ligands, tetrazole derivatives have been widely investigated in recent years in coordination polymer chemistry due to the excellent coordination ability of the four nitrogen atoms in the tetrazole group.[9] Simultaneously, there also were several examples, in which tetrazole derivatives act as complementary organic ligands to fabricate high-dimensional magnetic metal-azido networks.[8b-f] However, as far as we know, a complex that has both the parent tetrazolate and azide used together is not reported until now, although tetrazolate itself has rich coordination modes (Scheme 2) and can be used as a nice organic linker for transferring magnetic coupling. On the other hand, the combination of azide and tetrazolate anions in one complex could result in highly N-rich systems, which may be the good candidates of high energy materials. Herein, we report the tuned synthesis (Fig. 1), crystal structure, and magnetic properties of two new tetrazolate-azido-bridged Cu(II) coordination polymers: $[Cu(tz)(N_3)]_n$ (**1**) and $[Cu(tz)(N_3)(NH_3)_2]_n$ (**2**). Both **1** and **2** possess distinct 3D network structures being topologically described as a 3-connected *srs* ($SrSi_2$) type net and a 4-connected *cds* ($CdSO_4$) net, respectively, and show antiferrimagnetic properties.



Scheme1: Different bridging modes of azide anion.



Scheme 2: Different coordination modes of tetrazolate(tz) anion.

(Insert Fig. 1)

Experimental Section

Materials and general methods. All general reagents and solvents (AR grade) were commercially available and used as received. Distilled water was used in the hydrothermal synthesis. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a TENSOR 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. The powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the PXRD patterns were carried out by the single-crystal data and diffraction-crystal module of the *Mercury* program available free of charge *via* internet at http://www.iucr.org. Magnetic data were collected using crushed crystals of the sample on a Quantum Design PPMS-9T magnetometer. The data were corrected using Pascal's constants to calculate the diamagnetic susceptibility. During the magnetic measurement, the powder sample was enwrapped by a film and then fixed in the tube. The background of the film was corrected.

Synthesis of complexes

$[Cu(tz)(N_3)]_n$ (1). Complex **1** was prepared by the hydrothermal reaction: 10 mL of H_2O solution containing Htz (14 mg, 0.2 mmol), $CuCl_2·2H_2O$ (34 mg, 0.2 mmol), and sodium azide (20 mg, 0.3 mmol) was sealed in a 25-mL Teflon-lined stainless steel container and heated at 120 °C for 3 days. The black crystals were collected and washed with acetone, and then dried in air. (Yield: 31% based on $CuCl_2·2H_2O$). PXRD pattern and FT-IR spectrum of **1** are shown in Fig. S1 and Fig. S2, respectively in the Supporting Information. Anal. Calcd for $CHCuN_7$: C, 6.88; H, 0.58; N, 56.14. Found: C, 6.81; H, 0.61; N, 56.09.

$[Cu(tz)(N_3)(NH_3)_2]_n$ (2). 10 mL of ammonia solution containing Htz (14 mg, 0.2 mmol), $CuCl_2·2H_2O$ (34 mg, 0.2 mmol), and sodium azide (33 mg, 0.5 mmol) in a glass vial was left at room temperature and allowed solvent evaporate for three days. The black crystals were collected and washed with acetone, and then dried in air. (Yield: 28% based on $CuCl_2·2H_2O$). PXRD pattern and FT-IR spectrum of **2** are shown in Fig. S1 and S2, respectively in the Supporting Information. Anal. Calcd for CH_7CuN_9: C, 5.76; H, 3.38; N, 60.41. Found: C, 5.80; H, 3.43; N, 60.35.

Caution! Azide derivatives are potentially explosive, particularly in this highly N-rich system with metal ions. Although we have met no problems in handling the Cu(II) systems during this work, only a small amount of them should be prepared and managed with great caution, especially in the hydrothermal synthesis.

Single-crystal X-ray crystallography. Single-crystal X-ray diffraction data were collected on a Rigaku R-AXIS RAPID IP X-ray diffractometer equipped with a fine-focus sealed-tube X-ray source (graphite monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å). Suitable single crystals were directly picked up from the mother liquor, attached to a glass loop for data collection at 20 ^{o}C. Raw data collection and reduction were done using RAPID-AUTO and CrystalStructure softwares, respectively.[10] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package.[11] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of ligands were calculated in ideal positions with isotropic displacement parameters. CCDC-1052035 (**1**) and 1052036 (**2**) contain the supplementary crystallographic data for this paper. Crystallographic data and structural refinements, and selected bond distances and angles for **1** and **2** are listed in Table 1 and 2, respectively.

(Insert Table 1 and 2)

Results and Discussion

Synthesis and general characterizations. The complex **1** and **2** were synthesized as single crystals under different reaction conditions: the hydrothermal condition in water and at room temperature in ammonia solution, respectively through the reaction of $CuCl_2$, NaN_3, and Htz. As discussed below, **1** and **2** have different compositions and structures, demonstrating that the synthesis conditions have a great effect on the outcomes in this tetrazolate-azido system. We also checked the same reaction by the variations of solvents and reaction temperatures. For the water at room temperature, although we tried a lot of times under different conditions through changing the ratios of reactants and the concentration of the reaction system, we did not get a product which can be structurally characterized through single-crystal or powder X-ray diffraction at room temperature. In most cases, blue amorphous powders were obtained, which are difficult to determine their structures. With CH_3OH or CH_3CN acting as the solvent at room temperature and the higher temperatures of 60, 80, and 100 ^{o}C, respectively, again blue or green amorphous powders were obtained in each case, but not crystalline products. However, with the N,N-dimethylformamide (DMF), at both room and higher temperature up to 120 ^{o}C, no solid product formed, always gave a yellow or brown clear solution. For all obtained amorphous powders, we did not further analyze their structures in this work. The phase purity of the bulky products of **1** and **2** has been checked by PXRD. Fig. S1 shows the measured PXRD patterns of **1** and **2** and their simulated ones based on single-crystal structure analyses. It is obvious that the measured patterns match with the simulated ones, respectively, being indicative of pure products. The IR spectra (Fig. S2) of **1** and **2** show very strong absorption bands at 2092 and 2038 cm^{-1}, respectively which can be attributed to the asymmetric stretching vibrations of the coordinated azide ions. The absorption bands in 1000~1500 cm^{-1} range are of the characteristic of υ(C−N), υ(N−N), and δ(NNN) of the tetrazolate ligand.[12] The two complexes are stable in air at ambient temperature and insoluble in most solvents such as water, alcohol and acetone, indicating its polymeric nature as realized by the structural determination. In addition, due to their potential explosive nature (the N contents are as high as 50% and 60% in **1** and **2**, respectively), the thermal analyses of **1** and **2** were not carried out in this work.

Crystal structures. [Cu(tz)(N_3)]$_n$ (1). The single-crystal structural determination of complex **1** reveals that it is 3D coordination polymer and crystallizes in the orthorhombic space group $P2_12_12_1$. As shown in Fig. 2b, the crystallographic asymmetric unit of **1** consists of one Cu(II) cation, one tz anion, and one azido anion. Cu(II) ion adopts a five-coordinated configuration in a square-pyramidal coordination environment (Fig. 2a and b). The basal plane of square-pyramid consists of four nitrogen atoms, two from different tetrazole ligands [1.988(2) Å for Cu(1)–N(3D) and 1.990(2) Å for Cu(1)–N(4E)] and two from different azide groups [2.001(2) Å for Cu(1)–N(5) and 2.006(2) Å for Cu(1)–N(5F)]. The tz and azido groups occupy the opposite positions of the basal plane in the square-pyramidal environment. The apical position is occupied by nitrogen atom from a tetrazole ligand with an obviously elongated Cu–N bond [2.218(2) Å for Cu(1)–N(1)] (see Table 2). The Cu(II) center deviates from the mean equatorial plane by 0.2296(2) Å toward the apical site. In the structure, each azide anion links two Cu(II) atoms in a single end-on (EO) mode to form a *zig-zig* azide-bridged Cu(II) chain in the crystallographic *a* direction, with the Cu–N distances of 2.001(2) Å and 2.006(2) Å, respectively, being in the normal Cu–N ranges in EO azide-bridged Cu(II) chains.[13] In the chain, the Cu–N–Cu angle is 115.98(9)°, and the adjacent Cu···Cu separation is 3.3978(6) Å. The Cu···Cu distance is a little bit shorter than that in some single EO azide-Cu(II) chains,[2,3,13] probably due to the bridging of the tz groups. As additional bridges, each tz anion adopts 3-coordination mode (Mode IV in Scheme 2) to bond two adjacent Cu(II) ions of the azide-Cu(II) chain by use of two tz nitrogen atoms and to bridge another Cu(II) atom from different azide-Cu(II) chain. All tz groups are parallel to the *a* direction, but the tz groups bridge azide-Cu(II) chains in two different directions to finally form a 3D framework with small parallelogram channels running along the *a* direction (Fig. 2c). In the 3D framework, both tz and azide groups act as bridging ligands, so the whole 3D structure can be thought to be constructed through the Cu(II) centers coordinated simultaneously by μ-1,2,4 bridging tz ligands and μ-1,1 (EO) bridging azide anion (Fig. 2a). The bridging modes of azide and tetrazole ligands are significantly responsible for the magnetic properties of the complex as discussed in detail later.

Topologically, each tz ligand connects three adjacent Cu(II) ions through three Cu–N bonds, and simultaneously each Cu(II) ion links with three tz ligands. Thus, each tz ligand and Cu(II) ion can be defined as a three-connected node. As azide group only acts as an additional bridge, it is not necessary to consider it in the topological analysis. Based on this analysis, the structure of **1** can be described as a 3-connected *srs* ($SrSi_2$) type net with point symbol of $\{10^3\}$ (Fig. 2d).

(Insert Fig. 2)

$[Cu(tz)(N_3)(NH_3)_2]_n$ (2). The single-crystal structural determination reveals that **2** also has a 3D framework structure, but different from that of **1** and crystallizes in the monoclinic space group *C*2/*c*. As shown in Fig. 3b, the crystallographic asymmetric unit of **2** consists of half the Cu(II) center, half tz ligand, half azido anion, and one ammonia molecule. The Cu(II) center locates at an inverse center and takes a distorted octahedral coordination configuration finished by six nitrogen atoms (Fig. 3a and b). The four nitrogen atoms of the equatorial plane are from two tz ligands and two ammonia molecules with the Cu–N bond lengths being 2.038(2) Å and

2.011(3) Å, respectively. Two nitrogen atoms of distinct azide ions located on the two axis positions symmetrically, with a 2.493(4) Å Cu–N bond length (see Table 2). Due to the strong Jahn-Teller effect of Cu(II) ion, the Cu–N bond lengths in the axial positions are remarkably elongated, which would be significantly responsible for the magnetic properties as discussed later. As a whole, in **2** each tz ligand adopts a 2-coordination mode (Mode I in Scheme 2) to link two Cu(II) centers to form a tz-bridged Cu(II) chain, in which the intra-chain Cu···Cu distance is 6.061(3) Å. Each azide anion adopts a *trans*-μ-1,3 (EE) mode to bond two Cu(II) centers in two adjacent tz-bridged chains (giving a inter-chain Cu···Cu distance of 6.5580(9) Å), and each Cu(II) is thus linked by two tz and two azide groups. Interestingly, the azide groups bridge tz-Cu(II) chains in two different directions, to finally form a 3D framework with tetragonum channels along the *b* axis (Fig. 3c). It should be pointed out that, the μ-1,3 (EE) azido linker always links the metal centers in the most favorable *trans* fashion with a few exceptions showing a *cis*-type of coordination.[14]

From the viewpoint of structural topology, both azido and tz ligand act as linear bridges, the present framework of **2** can thus be described as a *cds* ($CdSO_4$) type net with point symbol of $\{6^5 \cdot 6^8\}$, based on the 4-connected Cu(II) centers (Fig. 3d).

(Insert Fig. 3)

Magnetic properties. Variable temperature susceptibility data for complex **1** were collected with an applied field of 0.2 T in the 300 to 2 K temperature range. χ_M vs T and $\chi_M T$ vs T plots can be found in Fig. 4a. The $\chi_M T$ value at room temperature is 0.33, slightly below the expected value for one Cu(II) ion with g = 2.0 (S = 1/2, g = 2.0, $\chi_M T$ = 0.375 cm^3 K mol^{-1}). As temperature decreases, so does the $\chi_M T$ product indicating antiferromagnetic interaction within the 3D network of **1**. The magnetization was measured at 2 K in the 0 to 5 T applied field range. As can be seen in Fig. 4b, it rises without reaching saturation. At 5 T the reduced magnetization value is 0.06, which supports the strong antiferromagnetic interactions dominant in **1**, leading to a diamagnetic ground state. The magnetic structure of **1** is formed by infinite chains of 5-coordinated Cu(II) ions with a square-pyramidal geometry bridged by EO azido ligands and tetrazolate ligands. Generally, the EO mode azido can mediate both ferro- and antiferromagnetic interactions depending on the Cu–N–Cu bond angle. For the Cu(II) system, it is observed that when this angle is less than 108^{o}, the complex shows ferromagnetic properties, and when it is larger than 108^{o}, the magnetic interaction between the paramagnetic centers is antiferromagnetic in nature.[15] In **1**, the Cu–N(N_3)–Cu angle is 115.98(9)^{o}, thus the coupling through the azido ligand should be antiferromagnetic.[16] The chains are linked into a square grid by tetrazolate ligands that mediate an interaction between the magnetic orbital (dx^2-y^2) of the Cu(II) ions in one chain with a full dz^2 orbital of the Cu(II) ions in the neighbouring chain.[17] This type of interaction is known to lead to weak ferromagnetic exchange. The magnetic susceptibility follows the Curie-Weiss law at temperatures above 100 K. Given the fact that the antiferromagnetic interaction along the chains will dominate the magnetic behaviour of **1**, the high-temperature data were modelled assuming isolated infinite chains. An equation for a infinite chain of Cu(II) ions[18] with S = 1/2 was used to fit the experimental susceptibility data above 100 K, the best fit is shown in Fig. 4a as a solid line and the fitting parameters were g = 2.2 and J = –41.0 cm^{-1}.

(Insert Fig. 4)

Fig. 5a shows the temperature dependence of the magnetic susceptibility of complex **2** at an applied DC field of 1.0 T in the 2 to 300 K range and at 500 G below 25 K. As can be seen in the plot of $\chi_M T$ per Cu(II) ion vs. T, there is no field dependence of the magnetic behaviour of **2**. As temperature decreases, the susceptibility per Cu(II) ion, χ_M, rises to a maximum at 23 K and then drops to a value of 0.004 cm^3 mol^{-1} at 2 K. The $\chi_M T$ product per Cu(II) ion has a value of 0.441 cm^3 K mol^{-1} at 300 K, well in agreement with an isolated Cu(II) ion. As temperature decreases, so does the $\chi_M T$ product, down to a value of 0.008 cm^3 K mol^{-1} at 2 K. The magnetization increases linearly to a value of 0.04 with field as this goes form 0 to 50000 G, never reaching saturation, as seen in Fig. 5b. All this clearly indicates antiferromagnetic interactions between the Cu(II) ions in **2**. The crystal structure shows a 3D arrangement of chains of Cu(II) ions linked by EE azide ligands; along the chains, each pair of Cu(II) atoms is bridged by a tetrazole. The EE azide bridges are known to lead to strong antiferromagnetic coupling but this is not the case in **2**, due to its particular structure. In **2**, each Cu(II) is 6-coordinated in a distorted octahedral fashion, the distortion takes the form of an very pronounced axial elongation along the dz^2 orbital, perpendicular to the Cu(II) magnetic orbital, dx^2-y^2. The Cu–N(N_3) bonds are always in this elongated axis (the Cu–N distance is 2.493(4) Å), thus, the interaction through this azide bridge is expected to be very weak or negligible. Along the chains, antiferromagnetic interaction can be predicted mediated by the tetrazole bridges, similar to that found in Cu(II) complexes with bridging imidazolate ligands[19] in which the bridging mode of the imidazolate is similar to that of tetrazolate in **2**. Taking all this into account, the system was treated as an isolated chain. The magnetic data above 20 K were fitted to simple 1D chain model[18] (the Hamiltonian is written as $\hat{H} = -2JS_1S_2$) and the inter-chain interactions were included in the model as a Curie-Weiss constant. A good agreement was obtained using the linear chain model of S = 1/2, and the best fit, shown in Fig. 5a as a solid line, was obtained for J = –8.62 cm^{-1}, g = 2.22, TIP = 37e-6 cm^3 mol^{-1} and a Curie-Weiss constant of –12 K.

(Insert Fig. 5)

Conclusion

In this work, through tuning reaction conditions, we have synthesized two novel tetrazolate-azido bridged Cu(II) coordination polymers with different 3D network structures. To the best of our knowledge, this is the first example of using parent tetrazole and azide together in preparing magnetic complexes. **1** features μ-1,1 (EO) azide and μ-1,2,4 tetrazolate coordination modes to link Cu(II) atoms to form a 3-connected *srs* ($SrSi_2$) type net, while **2** features μ-1,3 (EE) azide and μ-1,4 tetrazolate linkage modes to give a 4-connected *cds* ($CdSO_4$) type net. The two complexes show antiferrimagnetic properties, being well-correlated with their structures. This work extends the research of engineering azide-metal magnetic coordination polymer systems.

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Table 1. Crystal data and structure refinement parameters of **1** and **2**.

complex	**1**	**2**
Formula	$CuCHN_7$	$CuCH_7N_9$
Formula weight	174.63	208.70
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$
a, Å	6.7352(13)	11.804(2)
b, Å	7.5089(15)	5.7178(11)
c, Å	9.6823(19)	10.984(2)
α, °	90	90
β, °	90	115.84(3)
γ, °	90	90
V, Å^3	489.67(17)	667.2(2)
Z	4	4
D, g/cm^3	2.369	2.078
μ, mm^{-1}	4.353	3.221
Independent reflections	1117	585
R_{int}	0.0349	0.0357
R [$I/\sigma(\mathrm{I}) > 2$]	0.0169	0.0318
R_w [$I/\sigma(\mathrm{I}) > 2$]	0.0397	0.0893
Goodness-of-fit on F^2	1.148	1.142
No. reflection used	1117	585
No.Parameters refined	82	54
$\Delta\rho_{\text{max}}$ [e Å^{-3}]	0.230	0.970
$\Delta\rho_{\text{min}}$ [e Å^{-3}]	–0.464	–0.604

Table 2. Selected bond lengths (Å) and angles (°) of **1** and **2**.

$[Cu(tz)(N_3)]_n$ (**1**)			
Cu(1)–N(3)^{i}	1.988(2)	Cu(1)–N(4)^{ii}	1.990(2)
Cu(1)–N(5)	2.001(2)	Cu(1)–N(5)^{iii}	2.006(2)
Cu(1)–N(1)	2.218(2)	N(3)–Cu(1)^{iv}	1.988(2)
N(3)^{i}–Cu(1)–N(4)^{ii}	166.70(7)	N(3)^{i}–Cu(1)–N(5)	93.07(7)
N(4)^{ii}–Cu(1)–N(5)	86.33(8)	N(3)^{i}–Cu(1)–N(5)^{iii}	86.00(7)
N(4)^{ii}–Cu(1)–N(5)^{iii}	91.52(8)	N(5)–Cu(1)–N(5)^{iii}	166.63(3)
N(3)^{i}–Cu(1)–N(1)	93.58(8)	N(4)^{ii}–Cu(1)–N(1)	99.70(8)
N(5)–Cu(1)–N(1)	96.12(8)	N(5)^{iii}–Cu(1)–N(1)	97.25(8)
N(2)–N(1)–Cu(1)	114.1(1)	N(2)–N(3)–Cu(1)^{iv}	125.5(2)
N(4)–N(3)–Cu(1)^{iv}	122.9(2)	N(3)–N(4)–Cu(1)^{v}	118.4(2)
N(6)–N(5)–Cu(1)	122.0(2)	N(6)–N(5)–Cu(1)^{vi}	119.1(2)
Cu(1)–N(5)–Cu(1)^{vi}	115.97(8)		
$[Cu(tz)(N_3)(NH_3)_2]_n$ (**2**)			
Cu(1)–N(3)	2.011(3)	Cu(1)–N(1)	2.037(3)
N(3)^{i}–Cu(1)–N(3)	180.000(1)	N(3)^{i}–Cu(1)–N(1)^{i}	89.26(11)
N(3)–Cu(1)–N(1)^{i}	90.74(11)	N(2)–N(1)–Cu(1)	126.6(2)
N(3)–Cu(1)–N(1)	89.26(11)		

Symmetry mode for **1**: i –x + 2, y – 1/2, –z + 7/2; ii –x + 5/2, –y + 4, z – 1/2; iii x – 1/2, –y + 7/2, –z + 3; iv –x + 2, y + 1/2, –z + 7/2; v –x + 5/2, –y + 4, z + 1/2; vi x + 1/2, –y + 7/2, –z + 3. Symmetry mode for **2**: i –x + 3/2, –y + 3/2, –z + 2.

Captions to Figures

Fig. 1. The synthesis process of **1** and **2**.

Fig. 2. (a) Scheme showing the linkages of tz, Cu(II), and azide in **1**. (b) ORTEP view of the main unit of **1** with atom numbering scheme. (c) 3D network structure of **1** viewed along the crystallographic *a* axis, Cu(II) is shown as cyan, N of tz as gold, C as green, H as white, and azide as red. (d) Schematic representation of the topological net of **1** with tz being represented by 3-connected yellow spheres and Cu(II) by cyan.

Fig. 3. (a) Scheme showing the linkages of tz, Cu(II), and azide in **2**. (b) ORTEP view of the main unit of **2** with atom numbering scheme. (c) 3D network structure of **2** viewed along the crystallographic *b* axis, Cu(II) is shown as cyan, N of tz as gold, C as green, H as white, and azide as red. (d) Schematic representation of the topological net of **2** with Cu(II) being represented by 4-connected green spheres.

Fig. 4. (a) Temperature dependence of the magnetic susceptibility of **1** at an applied DC field of 0.2 T ($\chi_M T$, empty circles; χ_M, empty squares; the solid line is the best fit to the experimental data). (b) Field dependence of the magnetization of **1** at 2 K.

Fig. 5. (a) Temperature dependence of the magnetic susceptibility of **2** at an applied DC field of 1.0 T ($\chi_M T$, empty circles; χ_M, full circles; the solid line is the best fit to the experimental data). (b) Field dependence of the magnetization of **1** at 2 K.

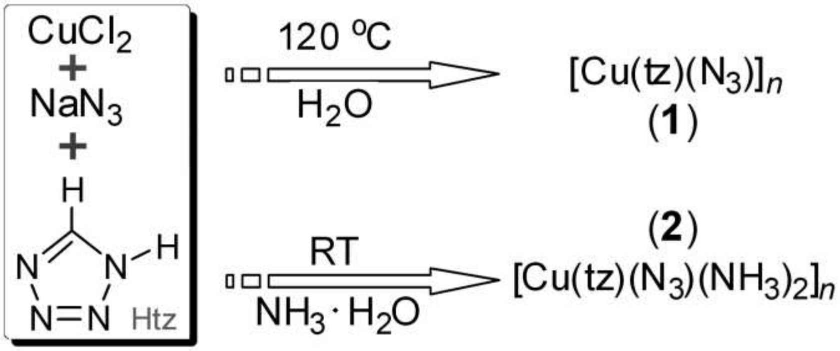


Fig. 1

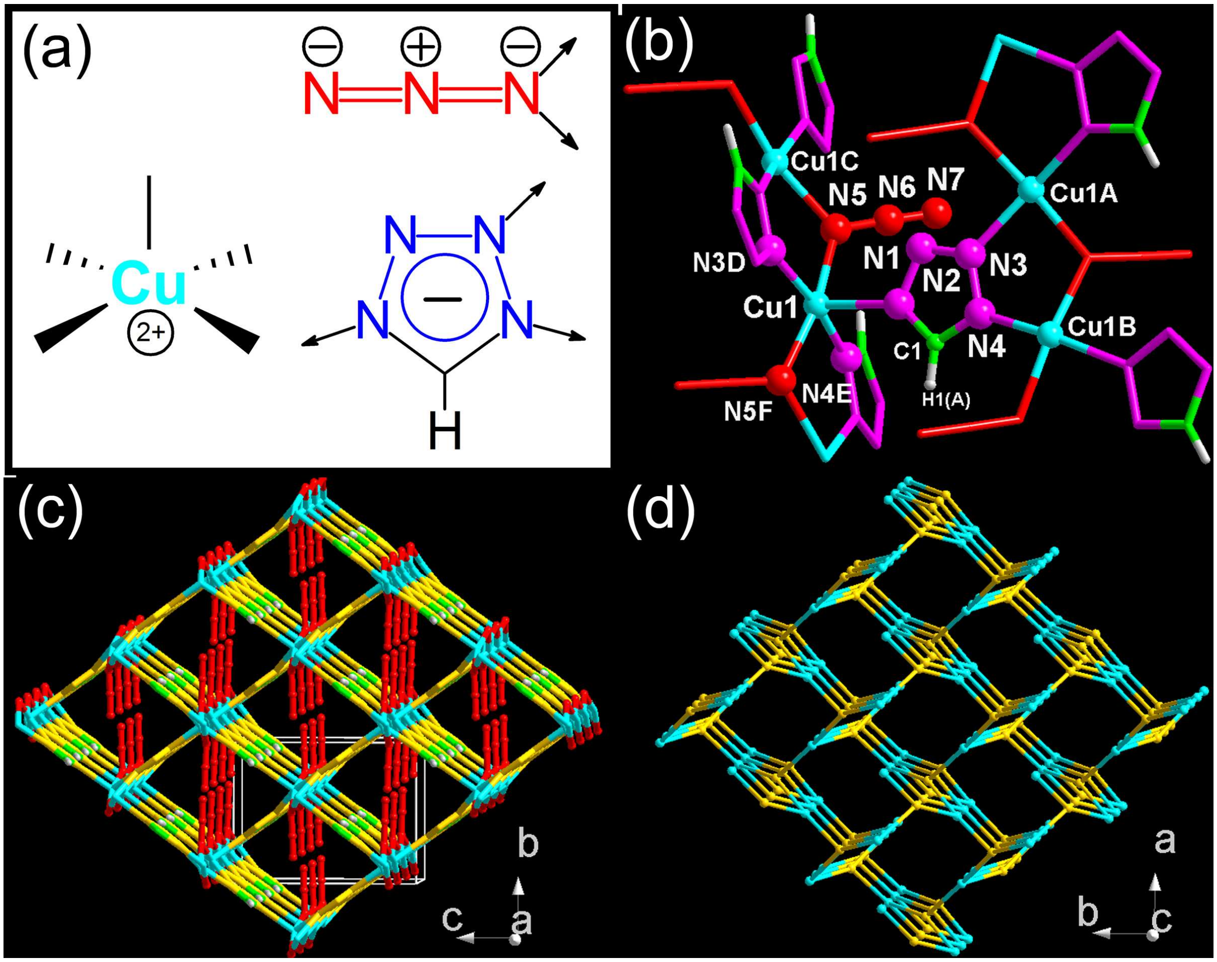

(a)
⊖ ⊕ ⊖
N=N=N
Cu
2+
N—N
N N
−
H
(b)
Cu1C
N5
N6
N7
Cu1A
N3D
N1
N2
N3
Cu1
Cu1B
C1
N4
H1(A)
N5F
N4E
(c)
b
c
a
(d)
a
b
c

Fig. 2

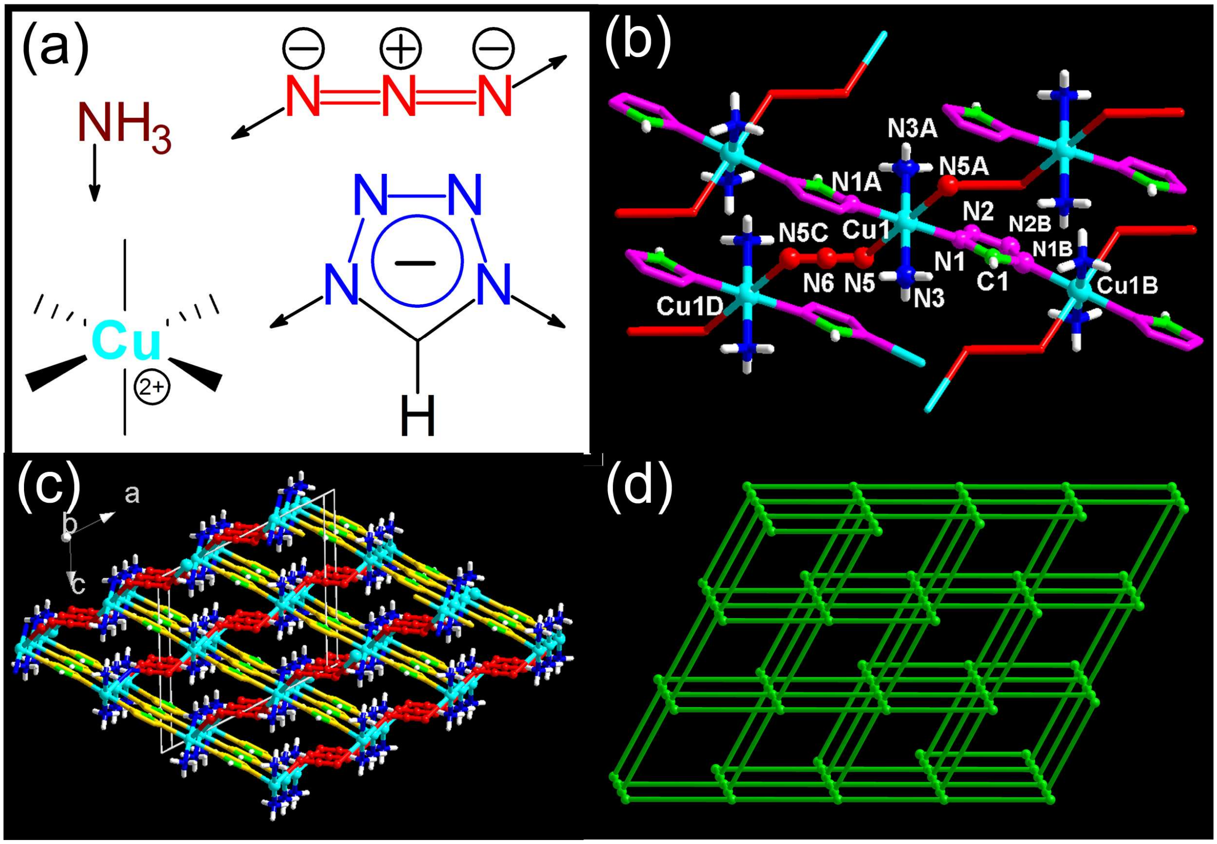
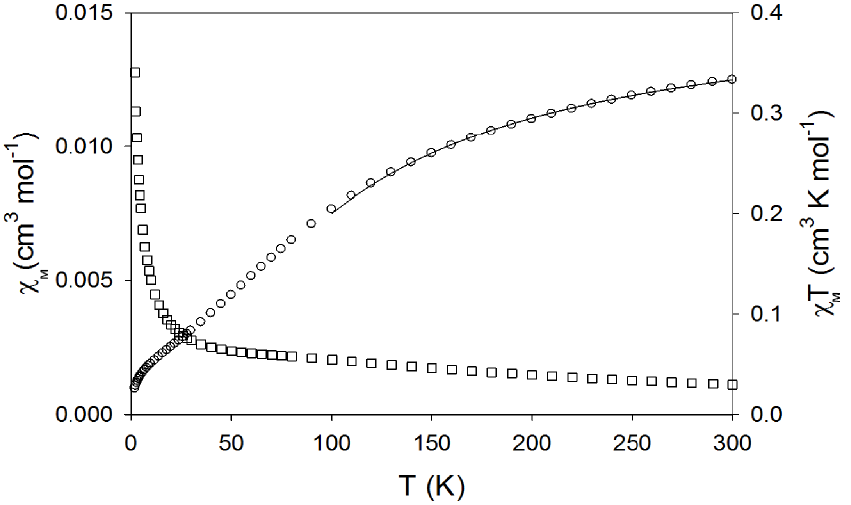

(a)
NH3
N=N=N
Cu
2+
N
N
N
N
H
(b)
N3A
N5A
N1A
Cu1
N2
N2B
N1B
N5C
N1
C1
N6
N5
N3
Cu1D
Cu1B
(c)
a
b
c
(d)

Fig. 3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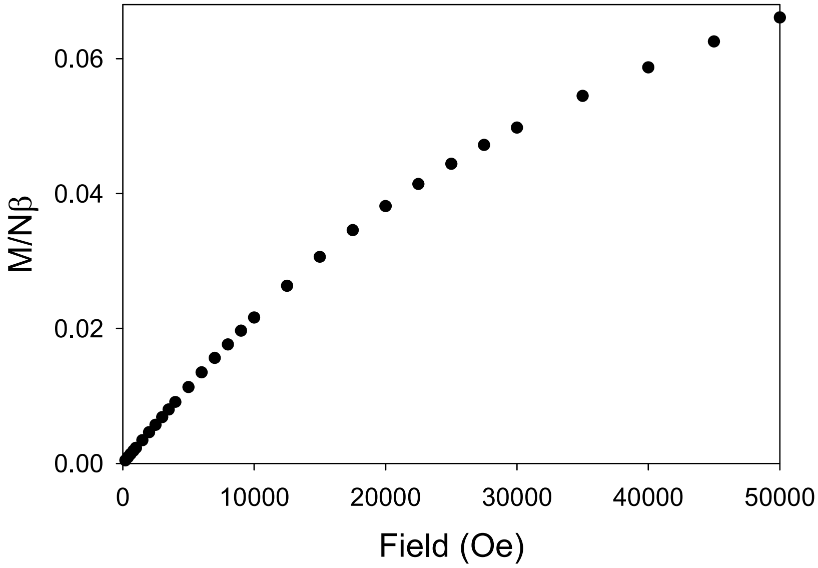
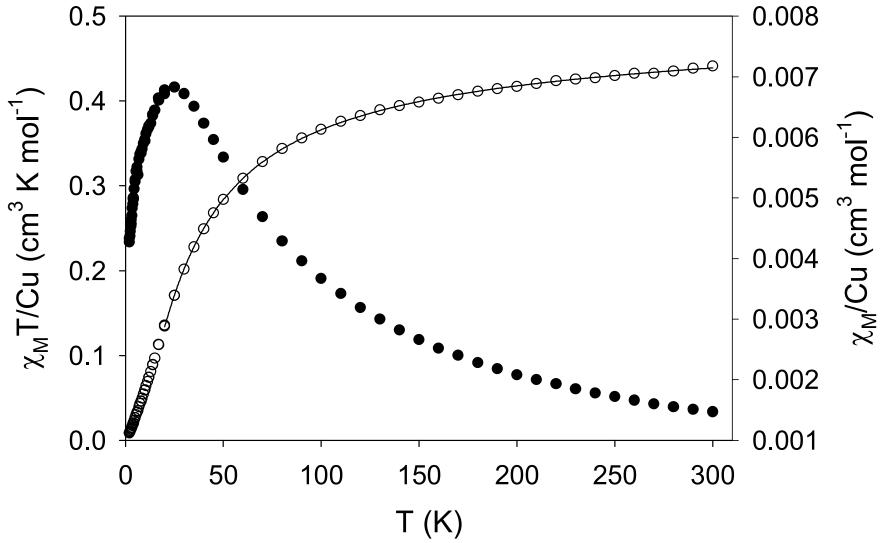
0.010
0.005
0.000
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
300
T (K)
χ_M (cm^3 mol^{-1})
χ_MT (cm^3 K mol^{-1})

(a)

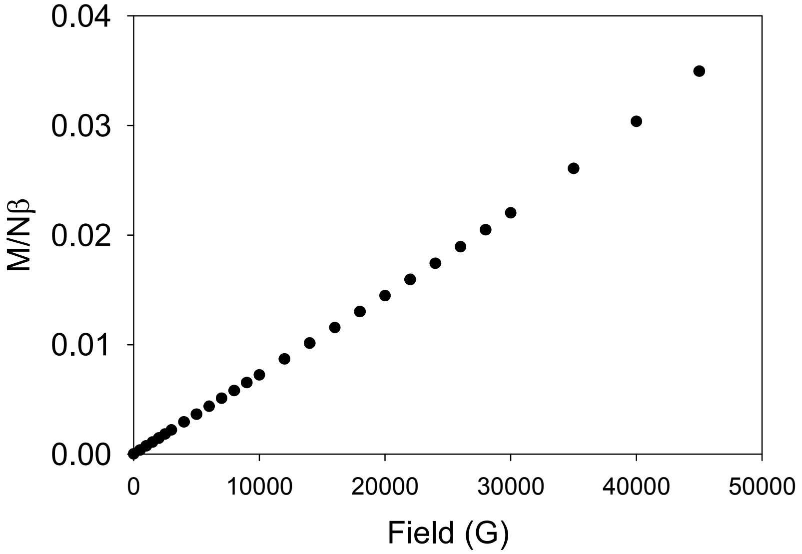

0.06
0.04
0.02
0.00
0
10000
20000
30000
40000
50000
Field (Oe)
M/Nβ

(b)

Fig. 4


0.5
0.4
0.3
0.2
0.1
0.0
$\chi_M T$/Cu (cm^3 K mol^{-1})
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
χ_M/Cu (cm^3 mol^{-1})
0
50
100
150
200
250
300
T (K)

(a)


0.04
0.03
0.02
0.01
0.00
M/Nβ
0
10000
20000
30000
40000
50000
Field (G)

(b)

Fig. 5

TOC

Tetrazolate-azido-copper(II) coordination polymers: tuned synthesis, structure, and magnetic properties

Ya-Bo Xie, Lei Gan, E. Carolina Sañudo, Haiyang Zheng, Jiongpeng Zhao, Minjian Zhao, Bin Wang and Jian-Rong Li

Two three-dimensional tetrazolate-azido-copper(II) coordination polymers, $[Cu(tz)(N_3)]_n$ (**1**) and $[Cu(tz)(N_3)(NH_3)_2]_n$ (**2**) were synthesized under different reaction conditions, hydrothermal for **1** and at room temperature in ammonia for **2**. Topologically, **1** can be described as a 3-connected *srs* ($SrSi_2$) net, while **2** is a 4-connected *cds* ($CdSO_4$) net. Magnetic measurements indicate that they have antiferrimagnetic properties.