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Coligand phenylacetic acid effect on structure and magnetic property of azido-bridged copper(II)-chains compounds

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Abstract

As for azido-copper(II) chains compounds, to explore and alter the structure as well as allow the influence of magnetic properties through substitutent in phenylacetic acid as coligand, three new azido-bridged Cu(II) compounds, [Cu(*o*-npa)(N_3)(H_2O)]$_n$ **(1),** [Cu(*p*-npa)(N_3)]$_n$ **(2)** and [Cu(*p*-mpa)(N_3)]$_n$ **(3)** (*o*-Hnpa = *o*-nitrophenylacetic acid, *p*-Hnpa = *p*-nitrophenylacetic acid, and *p*-Hmpa = *p*-methylphenylacetic acid), have been successfully obtained and structurally and magnetically characterized. Single-crystal structure analyses indicate that the azido ligands adopt single EO mode to connect the adjacent Cu(II) centers in all three compounds. In compounds **1** and **2,** the carboxylate groups exhibit the same μ_2-bridging bidentate mode. Although compound **2** present 2D layer-structure formed by *p*-NO_2 in aromatic ring connecting with 1D Cu(II)-chains, **2** show similar intrachain ferromagnetic coupling with **1**. When *p*-methylphenylacetic acid is employed as coligand, compound **3** exhibits 2D layer-structure, in which the carboxylate adopt μ_3-bridging tridentate mode to shorten the distance among Cu(II)-chains. Due to the countercomplementarity of the superexchange pathways in this system, compound **3** behaves as a magnet with spontaneous magnetization temperature of 7 K.

Introduction

In recent years, the field of molecular magnetism has been a hot research topic and achieved great progress.[1,2] The design and synthesis of molecule-based magnets especially one-dimensional (1D) magnets so-called single-chain magnets (SCMs) with organic bridging ligands and transition metals continues to be a productive area due to their intriguing structures, unique physical characteristics, and promising novel applications, such as magnetic sensors, magnetic switchers and multifunctional magnetic devices.[3,4] Coordination chemistry has been a powerful tool to access such systems, and a common strategy is to connect paramagnetic metal centers by short bridging groups ($C_2O_4^{2-}$, CN^-, SCN^-, N_3^-, etc.) to transmit magnetic coupling.[5] It has made a clear relationship between the coordination mode of azido and the way of transmitting coupling: μ-1,1 (end-on, EO) and μ-1,3 (end-to-end, EE) generally transmit ferromagnetic (FM) and antiferromagnetic (AFM) exchange interaction respectively, which is helpful to make the preliminary forecast of the magnetism of the certain compounds,[5] in spite of several exceptions.[6] In addition, plenty of compounds consist of other mixed azido bridging modes also show interesting magnetic properties.[7] Among metal-azido-bridged systems, the transition metal-azido-bridged compounds have drawn considerable attention, especially the Cu(II)-azido-bridged coordination polymers.[8] Recently, combining azido and coligand in one system is an interesting approach for constructing new structures and modulating magnetic behaviours.[9] Considering that the carboxylate group can also efficiently transmit magnetic exchange, introducing carboxylate in metal-azido system would increase structural diversity and modulate magnetic behaviors of the compounds, for example, pyridylcarboxylates,[10a] pyridylacrylates,[10b] pyridine carboxylate N-oxide,[10c] dicarboxylates,[10d] aromatic carboxylate derivatives,[11a] giving a large number of coordination polymers with diverse topologies and magnetic properties.[9] Similarly, non-coordinating substituents in the *o*, *m*, or *p* position of the aromatic ring of the coligand benzoic acid could exert influence on structures of the compounds, such as Cu···Cu distance, Cu-N-Cu angle, intrachain separation of Cu(II) ions, and further affect the magnetic behaviors of the compounds.[11] Extending the idea above, if phenylacetic acid is selected as coligand instead of benzoic acid, do the substituents in aromatic ring affect on the coordination mode of the carboxylate groups? Furthermore, what and how the intrachain structure and the magnetic behavior of the Cu(II)-azido system are changing?

In order to answer the questions above, three phenylacetates with *o*-nitro, *p*-nitro and *p*-methyl substituents as coligands were introduced into the Cu(II)-azido system. Herein we report the synthesis and characterization of three new azido-Cu(II) compounds which are respectively formulated as [Cu(*o*-npa)$(N_3)(H_2O)]_n$ **(1)**, [Cu(*p*-npa)$(N_3)]_n$ **(2)** and [Cu(*p*-mpa)$(N_3)]_n$ **(3)**. Compound **1** and **2**, in which nitro group located at *o* and *p* positions in phenylacetate acids, display similar intrachain structures with EO-azido and *syn*-*syn* carboxylate mixed-bridges. **1** is an infinite 1D chain, while **2** is of 2D layer-structure. Magnetic data indicate that both **1** and **2** represent intrachain ferromagnetic interactions. Interestingly, compound **3** behaves as a 2D ordered magnet with phase transition temperature about 7 K because carboxylate groups adopt μ_3-bridging tridentate mode derived from methyl group in phenylacetic acid.

Experimental section

Physical Measurements

Elemental analysis (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The FT-IR spectra were recorded in the range 400-4000 cm^{-1} using KBr pellets on an EQUINOX55 FT/IR spectrophotometer. The phase purity of the bulk or polycrystalline samples was verified by X-ray powder diffraction (XRPD) measurements performed on a Rigaku RU200 diffractometer at 60 kV, 300 mA and CuKα radiation ($\lambda = 1.5406$ Å), with a scan speed of 5° min^{-1} and a step size of 0.02° in 2θ. Temperature-dependent magnetic measurements were performed on a Quantum Design MPMS XL-7 SQUID magnetometer. Magnetic susceptibility measurements were collected in the range of 2-300 K, under an applied field of 1 kOe, and ac magnetization measurements were taken at 1.8 K from 0 to 50 kOe. All data were corrected for diamagnetism estimated from Pascal's constants, and an experimental correction for the sample holder was applied.

Materials and methods

All of the solvents and reagents for synthesis are of analytical grade and are commercially available. $CuCl_2·6H_2O$, *o*-nitrophenylacetic acid (*o*-Hnpa), *p*-nitrophenylacetic acid (*p*-Hnpa), *p*-methylphenylacetic acid (*p*-Hmpa) and NaN_3 were purchased from commercial sources and used without further purification.

Caution! Although we have not experienced any problems in our experiments, azido and its compounds are potentially explosive; only a small amount of material should be prepared and handled with care.

Synthesis

Preparation of $[Cu(o\text{-npa})(N_3)(H_2O)]_n$ (1)

Compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of $CuCl_2·6H_2O$ (0.0517 g, 0.3 mmol), NaN_3 (0.0196 g, 0.3 mmol), *o*-Hnpa (0.0908 g, 0.5 mmol) in 6 mL H_2O was sealed in a Teflon-lined stainless autoclave and heated to 140 °C. After being maintained for 72 h, then the reaction vessel was cooled to room temperature at 10 $°C·h^{-1}$. Large block dark green crystals were collected. Yield: 68% (based on Cu). *Anal.* Calcd. for $C_8H_8CuN_4O_5$ (%): C, 31.61; H, 2.63; N, 18.44. Found (%): C, 31.71; H, 2.59; N, 18.49. IR (KBr, cm^{-1}): 3497 (m), 2968 (s), 2085 (vs), 1684 (vs), 1568 (s), 1523 (s), 1394 (s), 1292 (w), 791 (w), 719 (m), 690 (w), 494 (w).

Preparation of $[Cu(p\text{-npa})(N_3)]_n$ (2)

A mixture of $CuCl_2·6H_2O$ (0.0342 g, 0.2 mmol), *p*-Hnpa (0.0362 g, 0.2 mmol), and NaN_3 (0.0131 g, 0.2 mmol) in 15 mL H_2O was stirred for 2 h at room temperature. A deep green solution was formed and filtered, then the filtrate was left to slowly evaporate at room temperature. Dark green crystals of **2** were obtained within two weeks. Yield: 52% (based on Cu). *Anal.* Calcd. for $C_8H_6CuN_4O_4$ (%): C, 33.60; H, 2.10; N, 19.60. Found (%): C, 33.56; H, 2.02; N, 19.69. IR (KBr, cm^{-1}): 3458 (m), 2916 (w), 2080 (vs), 1649 (s), 1551 (s), 1409 (s), 1229 (w), 732 (m), 598 (w), 534 (w).

Preparation of $[Cu(p\text{-mpa})(N_3)]_n$ (3)

The synthetic procedure for **3** is similar to **2** by replacing the *p*-Hnpa with *p*-Hmpa. Dark green crystals were collected in a week. Yield: 42% (based on Cu). *Anal.* Calcd. for $C_9H_9CuN_3O_2$ (%): C, 42.40; H, 3.53; N, 16.49. Found (%): C, 42.50; H, 3.46; N, 16.58. IR (KBr, cm^{-1}): 3447 (m), 2926 (w), 2093 (vs), 1634 (s), 1531 (s), 1400 (s), 1269 (w), 723 (m), 588 (w), 513 (w).

Crystallographic data collection and refinement

Suitable single crystals of five compounds were mounted on glass fibers for X-ray measurements. Reflection data were collected at room temperature on a Bruker SMART APEX-CCD-based diffractometer using graphite monochromated Mo K a radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[12] Data processing was accomplished with the SAINT processing program. The structures were solved by the direct methods and refined with full-matrix least-squares on F^2 using SHELXTL 97 program.[13] All non-hydrogen atoms were refined with anisotropic displacement parameters. Selected crystallographic data and structural refinement details for **1**, **2** and **3** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table S1-S3.

Results and discussion

Description of structures

Crystal structure of [Cu(*o*-npa)(N_3)(H_2O)]$_n$ (1)

Fig. 1

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit of **1** consists of one Cu(II) ion, one azido ligand, one *o*-npa ligand and one coordinated water molecule. As shown in Fig. S1(a), the Cu (II) ion is a slightly distorted octahedral geometry. The equatorial square is composed of two nitrogen atoms (Cu1-N1 = 2.004 Å, Cu1-N1A = 2.021 Å) from two azido ligands and two oxygen atoms (Cu1-O1 = 1.922 Å, Cu1-O1A = 1.939 Å) from two carboxylate groups of *o*-npa ligands. The apical positions are occupied by two oxygen atoms (Cu1-O2 = 2.807 Å, Cu1-O2A = 2.427 Å) from two coordinated water molecules. Adjacent Cu(II) ions are bridged by EO-azido, μ_2-bridging bidentate carboxylate bridges and water oxygen atoms with Cu-N-Cu angle of 110.3°, Cu-O-Cu angle of 77.9° and the Cu···Cu distance of 3.303 Å to form an isolated 1D carboxylate/EO-azido/H_2O mixed-bridged copper chain along the *b* direction (Fig. 1).

Crystal structure of [Cu(*p*-npa)(N_3)]$_n$ (2)

Fig. 2

Compound **2** crystallizes in the triclinic space group *P*-1 and contains two types of crystallographically independent Cu(II) ions, Cu1 and Cu2, each lying at an inversion center but possessing different geometries. As illustrated in Fig. S1(b), Cu1 adopts a slightly distorted octahedral geometry, while Cu2 takes a square-planar environment. The equatorial plane of Cu1 consists of two nitrogen atoms (Cu1-N1 = 1.917 Å, Cu1-N1A = 1.917 Å) from two equivalent single EO mode azido ligands, two oxygen atoms (Cu1-O1 = 1.917 Å, Cu1-O1A = 1.917 Å) from two equivalent carboxylate groups. Two nitro oxygen atoms (Cu1-O2 = 2.514 Å, Cu1-O2A = 2.514 Å) from another two *p*-npa ligands occupy the axial sites. Cu2 is equatorially coordinated by two nitrogen atoms (Cu2-N1A = 1.993 Å, Cu2-N1B = 1.993 Å) from two azido ligands and two oxygen atoms (Cu2-O3 = 1.934 Å, Cu2-O3A = 1.934 Å) from two carboxylate groups. In **2**, one carboxylate group of ligand bridges two Cu(II) ions by a μ_2-bridging bidentate mode. Unlike compound **1**, one nitro group of the *p*-npa ligand binds another Cu(II) ion by a monodentate mode. It may attribute to steric hindrance effect resulting from the different positions of the nitro group. The metal ions alternate in the Cu1-Cu2-Cu1 sequence to generate a 1D carboxylate/EO-azido mixed-bridged chain along the *a* direction (Fig. 2) in **2**. The intrachain Cu···Cu separation is 3.393 Å, and the Cu1-N1-Cu2 angle is 120.4°, which is much larger than the 108° of the Cu-N-Cu angle in other Cu(II)-EO-azido systems.[5*c*,8*b*,11*a*,14,15] Furthermore, these neighbor chains are cross-linked by the coordinated nitro groups from the *p*-npa ligands to afford a 2D layer along the *ac* plane (Fig. S2), with the nearest interchain Cu···Cu separation of 10.375 Å spanned by the *p*-npa ligands.

Crystal structure of [Cu(*p*-mpa)(N_3)]$_n$ (3)

Fig. 3

Fig. 4

Although obtained by the same synthetic method, compound **3** displays an entirely different structure compared to **2**. The single-crystal X-ray diffraction analysis suggests that compound **3** crystallizes in the monoclinic space group *P*2_1/c and adopts a 2D coordination network structure. The asymmetric unit is built up from one Cu(II) ion, one azido ligand and one *p*-mpa ligand. All Cu(II) ions are five-coordinated with a slightly distorted square-based pyramid geometry (Fig. S1(c)). The apical position of Cu1 is occupied by one oxygen atom (Cu1-O1 = 2.594 Å) from one carboxylate group, and the equatorial plane is formed by two oxygen atoms (Cu1-O2 = 1.926 Å, Cu1-O3 = 1.960 Å) from another two carboxylate groups and two nitrogen atoms (Cu1-N1 =1.979 Å, Cu1-N1A =1.973 Å) from two azido ligands. Single EO-azido and carboxylate bridges link two Cu(II) ions to form a 1D Cu(II) chain (Fig. 3), in which the Cu1-N-Cu1A angle is 122.4° and Cu1···Cu1A distance is 3.463 Å. Furthermore, the carboxylate groups link Cu1B ions in these 1D Cu(II) chains to form a 2D coordination network (Fig. 4). The carboxylate group adopts the μ_3-bridging tridentate coordination mode, which largely lessen the distance between two neighbour chains. The nearest separation of Cu(II) ions between two neighbor chains is 3.662 Å. For **3**, the methyl groups from *p*-mpa ligands affect the coordination mode of the carboxylate groups and the conformation of the 2D layers compared to **1** and **2**, which may stem from the electronic effect of the substituent of the coligand.

Magnetic Studies.

Crystalline samples of **1-3** were all pure-phase, as confirmed by XRPD (see Fig. S3 in the Supporting Information). According to the obtained data, a dominant ferromagnetic coupling between the Cu(II) ions in compounds **1**-**3** can be suggested.

Magnetic properties of [Cu(*o*-npa)(N_3)(H_2O)]$_n$ (1)

Fig. 5

The magnetic property of **1** under the form of $\chi_M T$ versus T plots (χ_M is the molar magnetic susceptibility per Cu(II) ion) is shown in Fig. 5. The $\chi_M T$ value at 300 K is equal to 0.55 cm^3 K mol^{-1}, which is higher than the expected value (0.375 cm^3 K mol^{-1}) of magnetically isolated Cu(II) ion (S = 1/2, g = 2.0). Upon cooling, the $\chi_M T$ value increases smoothly from room temperature until 50 K and then sharply reaches a maximum value of 6.86 cm^3 K mol^{-1} at 2.58 K. Eventually, it decreases rapidly up to 6.40 cm^3 K mol^{-1} at 2 K. This kind of curve is a typical signature of a strongly ferromagnetic coupling between the Cu(II) ions, noticeably at very low temperatures. The final decrease of $\chi_M T$ may be attributed to the saturation effect or the presence of interchain AFM interactions. The data above 70 K follow the Curie-Weiss law with a Curie constant C of 0.55 cm^3 K mol^{-1} and a Weiss constant Θ of 37.68 K (Figure 5, inset). The positive Θ value confirm the ferromagnetic coupling between Cu(II) centers, and the C value fall in the usual ranges expected for Cu(II) ions. The magnetic data of **1** is fitted using the following equation:[7]

$$\chi = \frac{Ng^2\beta^2}{4kT}\left[\frac{1+5.7979916x+16.902653x^2+29.376885x^3+29.832959x^4+14.036918x^5}{1+2.7979916x+7.008678x^2+8.6538644x^3+4.5743114x^4}\right]^{2/3} \tag{1}$$

$$\chi_{\mathrm{M}}T = \frac{\chi T}{1-(zJ'/Ng^2\beta^2)\chi} \tag{2}$$

$$x = J/2kT \tag{3}$$

The best fitting for the magnetic susceptibility data resulted in $g = 2.26$, $J = 35.44$ cm^{-1}, and $zJ' = -0.13$ cm^{-1} (zJ' describes the interchain antiferromagnetic interaction). The large J value confirms the strong ferromagnetic coupling between the Cu(II) centers, while the small negative zJ' value indicates the presence of weak interchain AFM interactions with long interchain distance, consistent with the drop of the $\chi_{\mathrm{M}}T$ product at low temperature. Magnetizations versus field data at 2 K are collected for **1** (Fig. S4). The M value increases very rapidly in the low field region and rises gradually as the field increases, and reaches to a saturation value of 1.18 Nβ at the higher fields, as expected for one Cu(II) ion with $g = 2.0$, demonstrating ferromagnetic coupling along the Cu(II) chain. To corroborate the existence of ferromagnetic long-range ordering, measurements of the ac susceptibility and hysteresis loop were made, but show negative results.

According to the structural data, the system can magnetically be treated as an infinite uniform chain in which magnetic coupling is mediated through the triple bridges (one EO-azido, one *syn-syn* carboxylate and one coordinated water molecule bridge). For the *syn-syn* carboxylate, it is well known that such bridge can transmit AFM interactions between neighbour metal ions.[7] The magnetic coupling pathway, EO-azido, is certainly one of the most interesting magnetic couplers in molecular magnetism, whose magnitude of J parameter depends on several factors, mainly the Cu-N-Cu angle (θ). The single EO azido bridge should also mediate FM coupling according to a number of studies on Cu(II) systems with such bridges. According to the previous reports,[8] EO-azido bridging Cu(II) ions with lower θ mediates a ferromagnetic coupling, but antiferromagnetic if the angle is above a critical θ value, which has been evaluated to be about 108°.[5c,8b,11a,14,15] However, compound **1** displays a ferromagnetic behaviour with the Cu-N-Cu angle of 110.3°, which is similar to some refuted reports.[11a] For two metal ions linked by multi-bridges, the overall coupling cannot be simply described as an algebraic sum of contributions arising from each bridge, which may exhibit the countercomplementarity of the superexchange pathways in such systems.[16,17,18] Thus the AFM contributions of each bridge in **1** cancel each other, resulting in strong intrachain FM exchange between the Cu(II) ions.

Magnetic properties of [Cu(p-npa)(N_3)]$_n$ (2)

Fig. 6

The magnetic behaviour of **2** is similar to that of **1**, also suggesting ferromagnetic coupling. As shown in the fig. 6, the $\chi_M T$ value per Cu(II) at room temperature is about 0.40 cm^3 K mol^{-1}, close to the value expected for a magnetically isolated Cu(II) ion. As the temperature is lowered, the $\chi_M T$ values increase smoothly to maxima about 5.095 cm^3 K mol^{-1} at 3 K, and then decrease rapidly to 4.266 cm^3 K mol^{-1} at 1.8 K. This indicates that the magnetic interaction among the Cu(II) centers is ferromagnetic, which is further confirmed by a positive Weiss constant Θ of 19.66 K and the Curie constant C of 0.365 cm^3 K mol^{-1} via the fit of the Curie-Weiss law above 25 K (Fig. 6, inset). Considering the interchain magnetic interactions through the long *p*-npa ligand should be much weaker than the intrachain interactions through the short (EO-azido)(*syn-syn* carboxylate) bridges, the 2D structural framework can be regarded as quasi-1D chains from a magnetic viewpoint.[19] Thus, using the same simulate equation like **1**, the fit result yields g = 2.28, J = 52.25 cm^{-1}, and zJ' = -0.36 cm^{-1}. The positive J value can be interpreted as a consequence of the existence of the EO-azido bridges, which gives ferromagnetic coupling. The small negative zJ' value indicates the presence of interchain antiferromagnetic interactions, consistent with the drop of the $\chi_M T$ value at 1.8 K. The reduced magnetization is shown in Fig. S5. Magnetization rises very fast as the field increases and tends to saturation at the higher fields, as expected for one Cu(II) ion. Indeed, the rapid and abrupt increase of the M/Nβ at low field indicates a ferromagnetically ordered state. No hysteresis was observed, and ac magnetic measurements revealed no out-of-phase ac susceptibility signals (Fig. S6 in support information), suggesting no indications of long-range ordering or SCM behaviours.

In compound **2**, actually, the 2D layers consist of 1D chains cross-linked by the ligands, in which the 1D chains made by the double bridges with one *syn-syn* carboxylate bridge and one symmetric EO-azido bridge linking two consecutive Cu(II) ions. Magnetically, the system can be treated as a uniform chain in which magnetic exchange is mediated through the (EO-azido)(*syn-syn* carboxylate) double bridges in spite of the adjacent Cu(II)-chains connected by the nitro groups. The nearest interchain Cu···Cu separation spanned by the *p*-npa ligands is 10.375 Å. In general, the EO-azido bridge will mediate a ferromagnetic exchange, while the *syn-syn* carboxylate will provide a pathway of antiferromagnetic coupling between the Cu(II) centers. However, compound **2** seems also in disagreement with the expectation mentioned above, which exhibits intrachain ferromagnetic exchange between the Cu(II) ions (J = 52.25 cm^{-1}). With the expansion of the distance between two chains, the interchain antiferromagnetic coupling is weak. In **2**, the Cu-N-Cu angle of the EO-azido bridge is 120.4°, which is much larger than the above-mentioned range of bond angles,[5c,8b,11a,14,15] giving the overall ferromagnetic behaviour.

In addition, the J parameter confirms that ferromagnetic interactions are mediated by the single EO-azido bridges in compound **2**.

Magnetic properties of [Cu(*p*-mpa)(N_3)]$_n$ (3)

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Compound **3** is remarkably different from **1** and **2** in magnetic behaviours. The temperature dependence of $\chi_M T$ for compound **3** as a $\chi_M T$ versus T plots is shown in Fig. 7. The value of $\chi_M T$ at 300 K is 0.534 cm^3 K mol^{-1}, larger than the predicted 0.375 cm^3 K mol^{-1} corresponding to an isolated Cu(II) ion (S = 1/2) with g = 2.0. As the temperature is lowered from room temperature, the $\chi_M T$ value continuously increases to reach a maximum value of 1.418 cm^3 K mol^{-1} at 18 K and then it decreases rapidly up to a value of 0.424 cm^3 K mol^{-1} at 1.9 K, which is attributed to zero-field splitting of Cu(II) ions or AFM interaction between the chains. As the temperature decreases, the $\chi_M T$ product increases, indicating ferromagnetic coupling between the Cu(II) ions within the chain in **3**. The Curie-Weiss fit of χ_M^{-1} above 60 K results in a Curie constant C = 0.48 cm^3 K mol^{-1} and Weiss constant Θ = 33.45 K (Fig. 7, inset). The positive Θ value suggests the presence of dominant ferromagnetic coupling between Cu(II) ions. Within this compound, the mainly Cu-bridge-Cu coupling pathway is listed below: Cu1-N1-Cu1A, Cu1-(COO)-Cu1A, Cu1A-O2-Cu1B. With no appropriate magnetic model for such a compound system with various bridges, it is difficult to simulate it and calculate the J values from experimental data. At 1.8 K, the field-dependent magnetization was increasing linearly to a maximum value of 0.75 Nβ (Fig. S7), indicating the magnetic moment is still unsaturated (the expected saturated value is $M_s = nSg$ = 1 Nβ). This behaviour is probably due to the significant antiferromagnetic interactions between the Cu(II) ions since the Cu(II) ions are not so anisotropic.[20] The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements were performed at a low applied field of 10 Oe in the temperature range of 1.8-10 K (Fig. 8). The data showed divergence below 7 K and the magnetization increases continuously with decreasing temperature. To corroborate the existence of ferromagnetic long-range ordering, measurements of the ac magnetic susceptibility and hysteresis loop were also made for **3**. The ac susceptibility measurements are performed in the range 1.8-10 K and frequencies of 1, 10, 100 and 1000 Hz. The figure showed a peak in the in-phase (χ'_{M}) signal and an out-of-phase (χ''_{M}) signal that is nonzero below 7 K, defining T_{c} for this magnet (Fig. 9). No frequency dependence was observed in the ac measurements, thus excluding any glassy behaviour in compound **3**. Furthermore, as shown in the Fig. 10, the hysteresis magnetization is measured at 2 K, 4 K and 10 K within ± 6 kOe. A characteristic hysteresis loop is observed a narrow gap at 4 K, which strongly supports the ferromagnetic ordering of **3** in the bulk.

For **3**, the methyl groups of the coligand affect the linkage of carboxylate groups thus the magnetic behaviour of the compound. Different from **1** and **2**, the chains are linked *via* the tridentate-bridged-carboxylate groups, which strengthen the global ferromagetic behaviour. Compared to **1** and **2**, the carboxylate groups in **3** largely lessen the distance between two neighbor chains with the nearest separation of Cu···Cu is 3.662 Å. According to the chain topology, there are three sets of magnetic exchange pathways: one *syn-syn* carboxylate bridge, one EO-azido bridge (intrachain) and two Cu-O-Cu bridges from two carboxylate groups (interchain). The antiferromagnetic coupling would be expected for **3** for the presence of EO-azido bridges displaying large Cu-N-Cu angle together with *syn-syn* carboxylate bridges featured in the chain. In fact, regardless of Cu-N-Cu bond angle (122.4°), there is an intrachain ferromagnetic coupling between the Cu(II) ions in **3**. Indeed, the strong ferromagnetic coupling behavior is similar to **1**. In a word, compound **3** behaves as a 2D ordered magnet.

To deduce general magneto-structural relationship, we have made a comprehensive comparison of Cu(II)-azido-benzoate compounds reported in recent years, as shown in Table S4. These compounds for the EO-azido with a Cu-N-Cu angles of 126.8°,[11a] 108.2°,[11a] 116.8°,[11a] 109.4°,[11c] 101.1°,[11c] 111.9°,[16] 105.5°[21d] exhibit strong ferromagnetic coupling. Similarly in our work, the Cu-N-Cu angles are 110.3°, 120.4° and 122.4°, which show ferromagnetic interactions. The coupling constant (*J*) values of compounds **1** and **2** are 35.44 cm^{-1} and 52.25 cm^{-1} respectively, which are close to the results in literatures.[11a,11c,16,21d]

Conclusions

Our interests are to probe how the flexible aromatic carboxylate ligands with different substituents as coligands influence the structure and magnetism in Cu(II)-azido compounds. Diverse structures and magnetic properties have been observed in the three compounds. Structural analyses show that compound **1** features a 1D three-fold bridged copper chain. Compound **2** displays the 2D layers in which the Cu(II)-azido chains are interlinked by nitro groups in *p*-npa ligands. Compound **3** shows a particular 2D layer in which the carboxylate groups adopt μ_3-bridging tridentate coordination mode. The magnetic investigations reveal that compounds **1** and **2** show dominant intrachain ferromagnetic coupling, while compound **3** represents magnet behaviour. The extension of carbon chain in aromatic phenylacetic acid has less influence on the coordination ability of the carboxylate group compared to benzoic acid. The different substituents in aromatic ring may fine-tune the structures and further affect magnetic properties of the compounds.

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† Electronic Supplementary Information (ESI) available: Selected bond lengths and angles are listed in Table S1-S3. Fig. S3 shows XRPD graphs of compounds **1**-**3**. CCDC reference numbers are 972618 (**1**), 972616 (**2**) and 972617 (**3**).

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Figure captions

Fig. 1 The Cu(II)-Chain with mixed water oxygen, carboxylate and azido bridges in compound **1**. Benzene rings and H atoms have been omitted for clarity.

Fig. 2 The uniform chain with mixed double bridges [(*syn*-*syn* carboxylate)(EO-azido)] in compound **2**. Benzene rings and H atoms have been omitted for clarity.

Fig. 3 The carboxylate/EO-azido mixed-bridge forms a 1D chain in compound **3**. Benzene rings and H atoms have been omitted for clarity.

Fig. 4 The μ_3-bridging tridentate carboxylate groups connect the adjacent chains forming a 2D sheet in compound **3**. Benzene rings and H atoms have been omitted for clarity.

Fig. 5 $\chi_M T$ *vs* T plot for compound **1**. The solid line is the fit to the experimental data. Inset: $1/\chi_M$ *vs* T plots, the red solid line is the best fit to the Curie-Weiss law.

Fig. 6 $\chi_M T$ *vs* T plot for compound **2**. The solid line is the fit to the experimental data. Inset: $1/\chi_M$ *vs* T plots, the red solid line is the best fit to the Curie-Weiss law.

Fig. 7 $\chi_M T$ *vs* T plot for compound **3**. The solid line is the fit to the experimental data. Inset: $1/\chi_M$ *vs* T plots, the red solid line is the best fit to the Curie-Weiss law.

Fig. 8 FC and ZFC plots at 10 Oe for compound **3**.

Fig. 9 χ'_{M} and χ''_{M} vs T plots for compound **3**.

Fig. 10 Hysteresis loop of compound **3**.

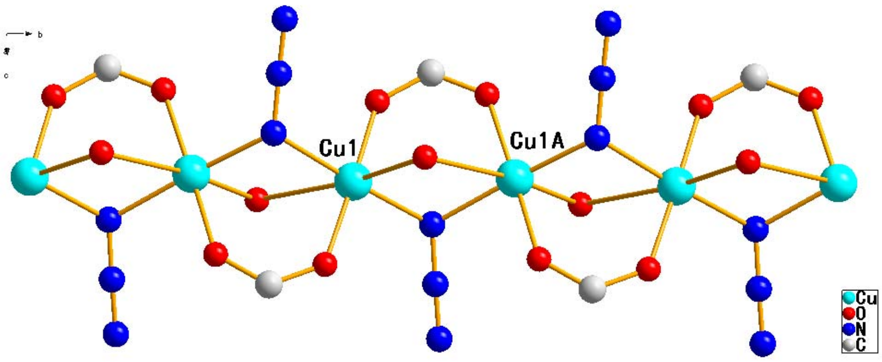


Fig. 1

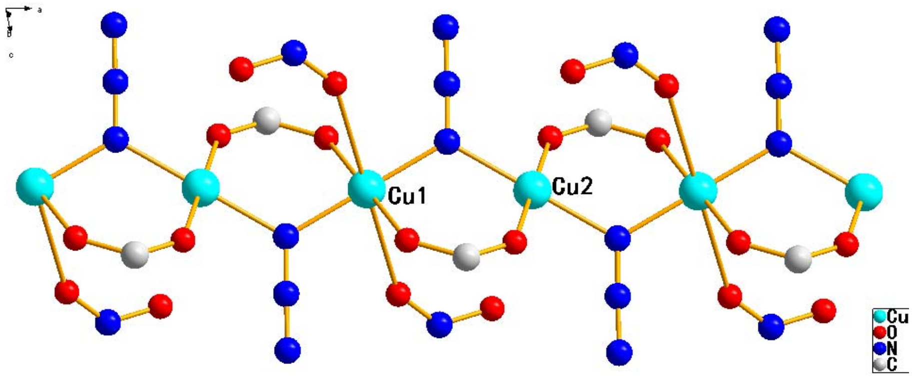
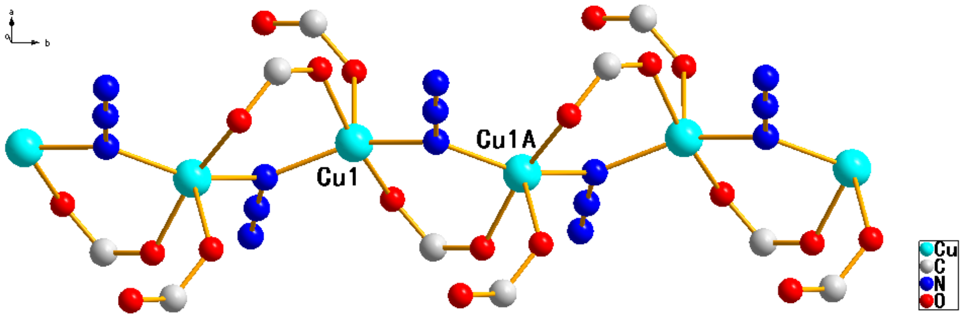


Fig. 2



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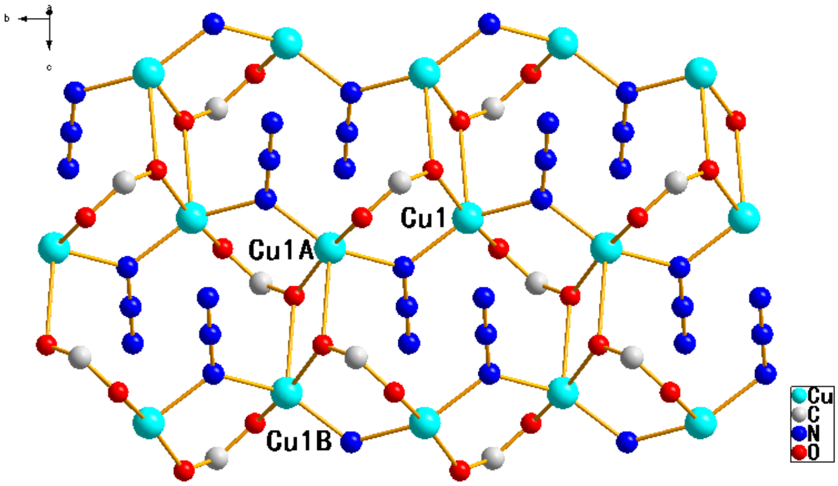

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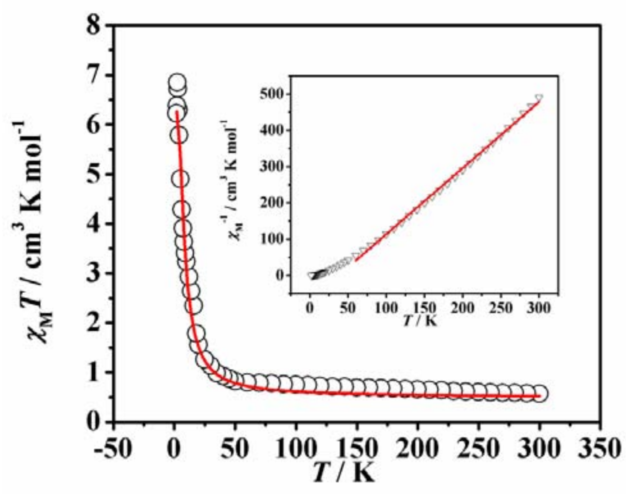

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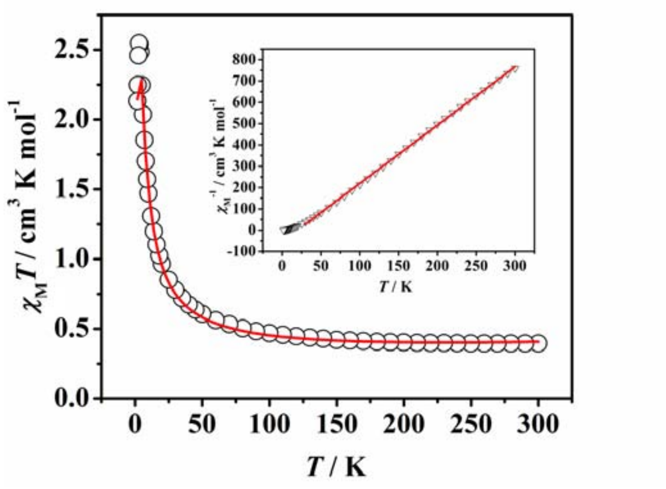

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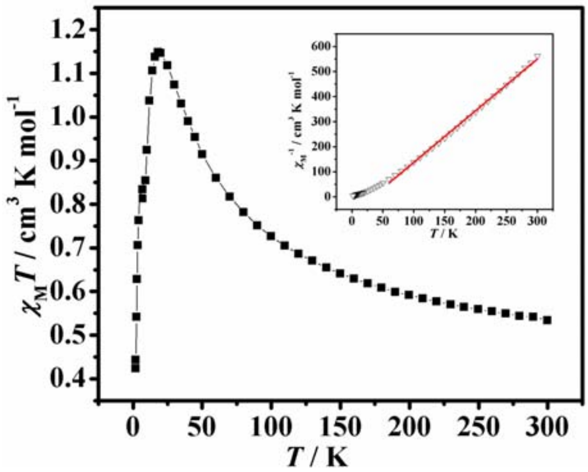

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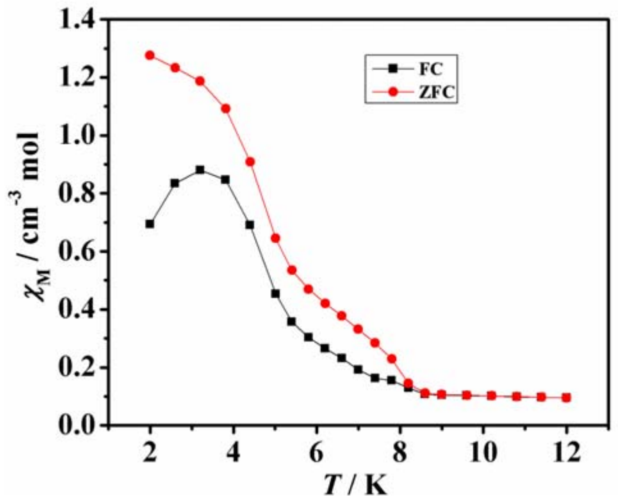

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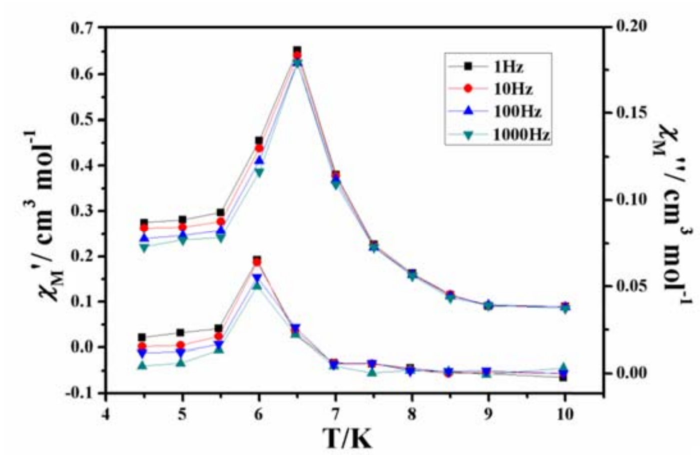

Fig. 9

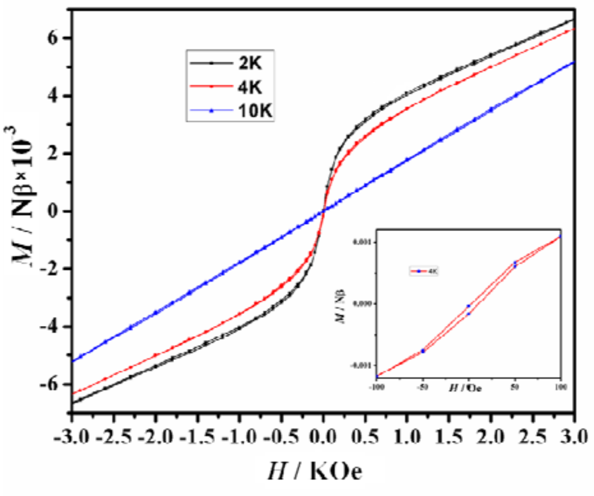

Fig. 10

Table 1 Selected crystallographic data for the three compounds **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_8H_8CuN_4O_5$	$C_8H_6CuN_4O_4$	$C_9H_9CuN_3O_2$
Formula weight	303.72	285.71	254.73
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$
a (Å)	13.5498(16)	6.785(5)	17.787(3)
b (Å)	6.5985(8)	7.594(6)	6.6764(13)
c (Å)	13.6226(16)	10.591(8)	8.4841(16)
α (°)	90	70.714(15)	90
β (°)	116.118(2)	77.11(14)	102.003(3)
γ (°)	90	88.869(14)	90
V (Å^3)	1093.6(2)	501.3(7)	985.5(3)
Z	4	2	4
D (g/cm^3)	1.845	1.893	1.717
Mu (mm^{-1})	2.018	2.188	2.197
$F(0\ 0\ 0)$	612	286	516
Unique reflections	1937	1736	1816
Observed reflections	5269	1736	4869
R_{int}	0.0358	0.0000	0.0696
Final R indices [$I > 2\sigma(I)$]	R_1 =0.0331 wR_2 =0.0795	R_1 =0.0858 wR_2 =0.1803	R_1 =0.0508 wR_2 =0.1210
R indices (all data)	R_1 =0.0439 wR_2 =0.0855	R_1 =0.1716 wR_2 =0.2360	R_1 =0.0907 wR_2 =0.1628
Goodness-of-fit on F^2	1.075	1.049	1.003

Coligand phenylacetic acid effect on structure and magnetic property of azido-bridged copper(II)-chains compounds

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