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Microwave-Assisted Stepwise Synthesis and Typically Metamagnetic Behavior of a Unique Two-Dimensional Net-Based Material Based on Linear Cu(II)-Azido Chains Mediated by Discrete Cu(II) Segments

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ABSTRACT: A unique two-dimensional layer-based material $[Cu(\mu_{1,1}\text{-}N_3)_2(H_2O)][CuL_2]$ (**1**, **L** = 2-methylpyrazine-5-carboxylate) was produced by a stepwise, microwave-assisted synthesis, featuring linear Cu(II)-$\mu_{1,1}$-azido chains mediated by discrete CuL_2 motifs. The mutual stabilization of the zero-dimensional and one-dimensional motifs in the unusual crystalline lattice of **1** is achieved by both coordination and supramolecular interactions. As a consequence, this material represents a novel copper(II)-based metamagnet resulting from the nature of the strong intrachain ferromagnetic coupling versus the weak interchain antiferromagnetic coupling.

In the realm of molecular magnetism, only a few magnetically ordered coordination complexes have been observed to exhibit metamagnetic phase transitions at low temperature.[1] In particular, homometallic metamagnets have been limitedly documented including metal phosphonates[2] or carboxylates[3,4] and azido-bridged complexes.[5] In these cases, metal ions with strong magnetic anisotropy, such as Co(II), and Ni(II), or weak magnetic anisotropy Mn(II) are usually involved in the resulting three-dimensional (3D) structures with diverse magnetic exchanges.[1−5] In contrast, only several copper(II)-based metamagnets are known so far.[5a,6] One reason is the exceptionally isotropic spins of Cu(II) and another pivotal reason may be the difficulty in synthesizing predictable copper(II)-based coordination polymers that display both strong ferromagnetic coupling and weak antiferromagnetic coupling.[1,7] As is well-known, coupling of the magnetic ordering is a consequence of the 3D crystalline structure, and complicated magnetic anisotropy has significant influence on the bulk magnetic property, in particular, the metamagnetic behavior. Thus, the design of extended homospin networks with predictable metamagnetic properties is still a great challenge in the field of molecular magnets.[4] As one of the most versatile ligands, the azido anion has been extensively used for obtaining magnetic systems with different dimensionality.[8,9] From the viewpoint of magneto-structural correlation, utilizing the various superexchange modes of the azido moiety and Jahn−Teller effect of Cu(II) in an elongated octahedral or square-pyramidal sphere may provide an opportunity for facing such a challenge.[10]

With regard to the synthetic aspects, the microwave heating technique has recently been introduced into the hydrothermal method, representing an extremely attractive route for preparing polymetallic complexes or coordination polymers,[11,12] benefiting from the higher yield, shorter reaction time, as well as the formation of unique crystalline products. On the other hand, in virtue of the stepwise synthesis approach, using multicomponent assemblies to design and prepare structurally controlled supramolecular systems via molecular recognition is also an interesting theme.[13] In this regard, by controlling over the relative disposition of the components in the final structures, the self-assembled processes as well as the structural and physical functionality may

be well dominated. Herein, we demonstrate the microwave-assisted, stepwise synthesis of a unique inorganic−organic hybrid material **1** (see Scheme 1),[14] consisting of one-dimensional (1D) linear chains of $[Cu(\mu_{1,1}\text{-}N_3)_2(H_2O)]_n$ and discrete (0D) planar $[CuL_2]$ segments (**L** = 5-methylpyrazine-2-carboxylate). Remarkably, this homospin Cu(II) supramolecular complex exhibits typically metamagnetic behavior.

As shown in Scheme 1, compound **1** was produced by a stepwise, microwave-assisted reaction of mononuclear precursor (**1′**)[15] with $Cu(NO_3)_2 \cdot 3H_2O$ in the presence of NaN_3 at 140 °C for a total of 30 min. The same products can be obtained when the reaction heating time is adjusted to 25 or 20 min (see Figure 1), but the total yield decreased from 30% to ∼22%. When the reaction heating time is 15 min or less, only a small amount of opacity, small coarse polycrystals appear, which are hardly suitable for single crystal X-ray analysis. Hence, the proper reaction heating time plays an important role in the formation of good single crystal qualities for **1**.

X-ray structural analysis of **1** shows that there are two independent Cu(II) ions per asymmetric unit,[16] with different coordination environments, being involved in two distinct coordination motifs $[CuL_2]$ and $[Cu(\mu_{1,1}\text{-}N_3)_2(H_2O)]_n$ (see Figure 2). In the centrosymmetric 0D motif $[CuL_2]$ (see Figure 2a), the N_2O_2 quadrangle coordination sphere of Cu1 is completed by two pyrazine nitrogen donors (Cu−N = 1.981(3) Å) and two carboxylate oxygen atoms (Cu−O = 1.936(2) Å) from two chelating **L** ligands.[15] This planar molecule, with vacant axial sites around the Cu(II) center, has the approximate size of ca. 9.38 × 7.17 Å and functionalizes as a suitable template molecule in this structure.

The copper(II)-azido moiety $[Cu(\mu_{1,1}\text{-}N_3)_2(H_2O)]_n$ shows a 1D linear array (see Figure 2b). The Cu2 ions here take a square pyramidal geometry, in which the equatorial plane consists of the four nitrogen atoms from four different $\mu_{1,1}\text{-}N_3$ anions, and the axial site is occupied by one water ligand (Cu−O = 2.186(2) Å). As a result, the Cu2 centers are doubly bridged by the $\mu_{1,1}$-azido anions to form straight chains that are parallel to the crystallographic a axis. As for the linear azido ligands (N−N−N bond angles = 177.5(1) and 178.3(1)°), the N−N distances binding to Cu(II) (N3−N2 and N6−N5) are 1.206(1) and 1.208(1) Å, whereas those of N2−N1 and N5−N4 are 1.141(1) and 1.133(1) Å. The Cu−N−Cu angles of 99.9(2)° and 98.6(1)° within the copper-azido chain are associated with the short Cu−N
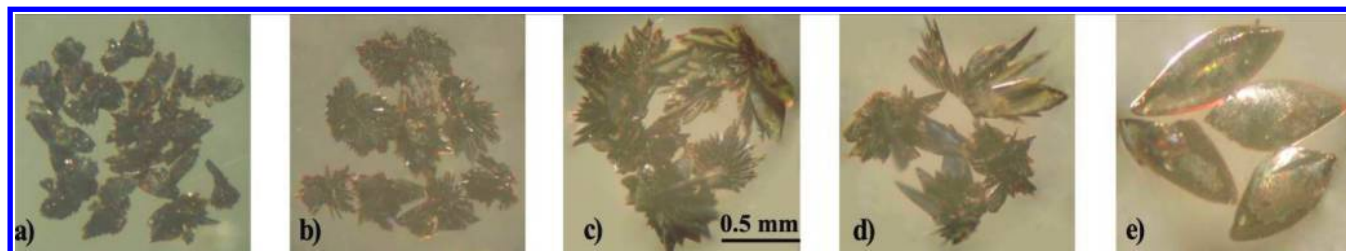
Figure 1. A series of optical microscope images with different reaction times assisted with microwave for **1**: (a) 10 min, (b) 15 min, (c) 20 min, (d) 25 min, (e) 30 min.
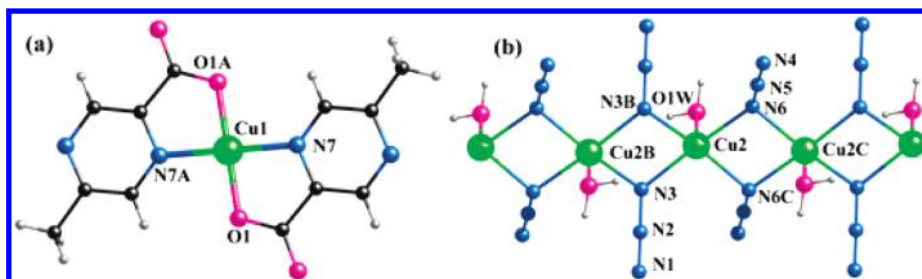

Figure 2. (a) The coordination environment of Cu1 in the discrete 0D component of **1**; (b) the coordination environment of the Cu2 in the 1D copper-azido component of **1** (symmetry code: $-x+1$, $-y$, $-z$ for a, $-x+1$, $-y-1$, $-z-1$ for b, $-x+2$, $-y-1$, $-z-1$ for c, part of H atoms omitted).

Scheme 1. Microwave-Assisted Stepwise Synthesized Approach for Compound 1 (L = 2-Methylpyrazine-5-carboxylate)

lengths (Cu−N = 1.990(3) and 2.022(3) Å), and the adjacent intrachain Cu···Cu distances are 3.057 and 3.062 Å.

Analysis of the crystal packing suggests that the [Cu-$(\mu_{1,1}$-N$_3)_2$(H$_2$O)]$_n$ chains are well separated with the shortest interchain Cu···Cu distance of ca. 10.66 Å,[9] and as a consequence, the discrete [Cu**L**$_2$] components occupy the void space between the [Cu($\mu_{1,1}$-N$_3)_2$(H$_2$O)]$_n$ motifs with the short Cu1···Cu2 distances of 5.716 and 5.531 Å (see Figure 3). Notably, the terminal N4 atoms of the bridging azido ligands in the 1D arrays are weakly interacted with the Cu(II) ions of [Cu**L**$_2$] from the axial positions (Cu1−N4 = 2.608(1) Å), with the Cu1−N4−N5−N6−Cu2 torsion angle of 93.7(8)°. Thus, considering such weak Cu−N coordination, the bridging fashion of azido can be regarded as μ_3-1,1,3 mode, which combine the 1D and 0D motifs into a 2D layered network. Weak interchain magnetic interactions through the μ_3-1,1,3-azido anions are expected, according to the reported examples with similar Cu···Cu distances and torsion angles.[8,9] In addition, the terminal coordinated water molecules from the straight 1D copper-azido chains are also strong hydrogen bonded to the carboxylate O2 atoms of [Cu**L**$_2$] with the O···O distance of 2.706 Å and the O−H···O angle of 162°. Furthermore, interlayer O−H···N and C−H···O hydrogen bonding between the pyrazine groups and water/carboxylate are also found, which lead to the formation a 3D supramolecular architecture (see S1, Table S3, Supporting Information).

Some interesting features are observed in the structure of **1**. The [Cu**L**$_2$] complex units can be considered as a new type of
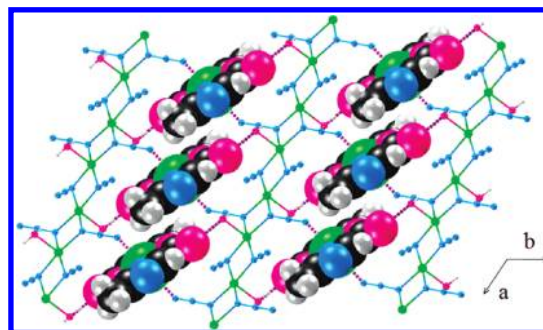

Figure 3. The 2D supramolecular layer consists of 0D and 1D component by weak Cu−N coordinated and hydrogen bonding interactions.

"metal-containing ligand",[14] which interconnect the [Cu($\mu_{1,1}$-N$_3)_2$-(H$_2$O)]$_n$ inorganic chains into a 2D hybrid network via weak coordination interactions and further into a 3D supramolecular framework via H-bonding. This represents a typical example for a supramolecular stabilizing effect via molecular recognition,[13] and the mutual stabilization is due to the cooperative effect of multiple interactions. In other words, the inorganic Cu−azido arrays are structurally directed by the discrete [Cu**L**$_2$] moieties, which undoubtedly will also influence the bulky magnetic behavior of **1**. On the other hand, although diverse polymeric structures have been observed in numerous metal-azido systems including

ancillary ligands,[17−19] to our knowledge, complex **1** is one of the very rare examples of 2D polymeric systems with double $\mu_{1,1}$-N_3 bridged linear chains linked by sole μ_3-1,1,3-N_3 bridges.[8,9] In fact, the success paradigm for assembly of such a coordination network from a predesigned complex precursor is quite unusual. The stepwise synthesis method described here offers an intermediate step from the 0D planar molecules, the chains toward the 2D networks, which thus is potentially useful for a systematic study of the relationship between the structure and metamagnetic property resulting from the strong intrachain ferromagnetic coupling versus the weak interchain and/or interlayer antiferromagnetic coupling.[8,9,19]

Magnetic susceptibility measurements were carried out by using a crushed single-crystal sample of **1** in the 2−300 K range at 1 KOe (see Figure 4). The $\chi_m T$ value of 1.5 cm^3 K mol^{-1} at 300 K is slightly higher than that expected for three uncoupled Cu(II) ions.[7] Upon lowering the temperature, the $\chi_m T$ increases gradually and then shows an abrupt rise below 22 K, up to the maximum value (34.4 cm^3 K mol^{-1}) at 5.6 K. The $1/\chi_m$ vs T plot (300−90 K) obeys the Curie−Weiss law with a positive Weiss constant θ of 34.92 K (see Figure S2, Supporting Information). These observations clearly indicate the dominating ferromagnetic coupling and also some characteristic of long-range magnetic ordering, resulting from the strong ferromagnetic interactions via double $\mu_{1,1}$-N_3 bridges.[7−9,18,19] The decrease of $\chi_m T$ at lower temperature (below 5.6 K) may arise from the saturation effect and/or antiferromagnetic coupling via weak exchange bridges. The magnetizations after zero-field-cooling (ZFC) and subsequent field-cooling (FC) reveal reversibility and non-bifurcation, confirming the long-range antiferromagnetic ordering below 6.4 K (see Figure S3, Supporting Information). The temperature dependence of the ac susceptibility measured in a field of 2.5 Oe shows the same features (see Figure 4 inset). The maximum value of χ' observed at 6.4 K agrees with the above results and confirms the occurrence of a phase transition. No obvious out-of-phase signal (χ'') is found below 6.4 K, revealing the lower dimensional magnetism, and no frequency dependence is observed in the ac measurement, which thus excludes any glassy behavior.

To prove the magnetic details of **1**, other dc curves were measured at low temperature. For applied fields below 1000 Oe, the field-cooled (FC) curves present a maximum at 6.4 K (see Figure 5), which thus indicates that some interchain and/or interlayer antiferromagnetic interactions may also be operative. However, a magnetic field above 1500 Oe is sufficient to overcome these weak couplings, and a field-induced transition from an antiferromagnetic to a ferromagnetic state is found. Interestingly, the magnetization curves for different temperatures (below the transition temperature) exhibit a sigmoidal shape with a common crossing point for $H = 1200$ KOe (see Figure 5 and 6). The isotherm at 2 K clearly indicates that the magnetization value is 3.24 $N\beta$ (see Figures 6 and S4), being slightly higher than the expected saturated value of three Cu(II) ions. The low-field magnetization presents a beautiful butterfly-shaped hysteresis around 1200 Oe (see Figure 5), which is in agreement with the results of FC. All of the measured data indicate that **1** is a metamagnet, and the critical field for the metamagnetic transition is ca. 1200 Oe at 2 K, resulting from the strong intrachain ferromagnetic coupling versus the weak interchain antiferromagnetic coupling (see Figure S5, Supporting Information).[4,9]

To model the magnetic properties of **1**, we also tried to use an approximate approach similar to that previously used for framework contained uniform Cu-azido chains.[20] Taking into account the magneto-structural correlation of **1**, the 3D supramolecular motif was roughly treated as a system of interacting chains. The uniform Cu-azido chains are separated by the mononuclear [CuL$_2$] motifs, where J and zJ' stand for the exchange integrals within and between the chains, respectively. The magnetic susceptibilities above 30 K were fitted to give the best parameters of
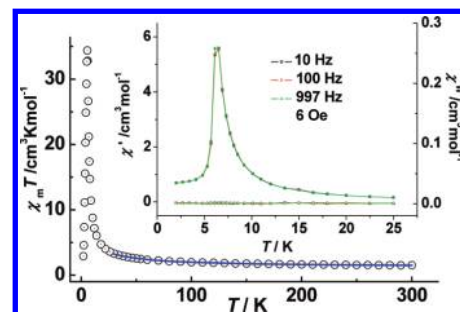

Figure 4. Plot of $\chi_m T$ versus T for **1**. The field strength used was $H = 1000$ Oe per {Cu(II)}$_3$; the solid lines represent the best fit to the (blue). Inset: the temperature dependence of the in phase (χ') and the out-of-phase (χ'') ac magnetic susceptibilities for **1**.
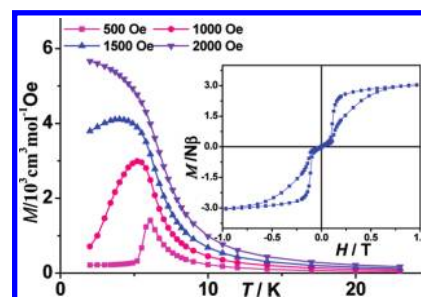

Figure 5. Plot of magnetization M versus T at 0.5, 1, 1.5, and 2 KOe for **1**; inset: the hysteresis loop for **1** at 2 K.
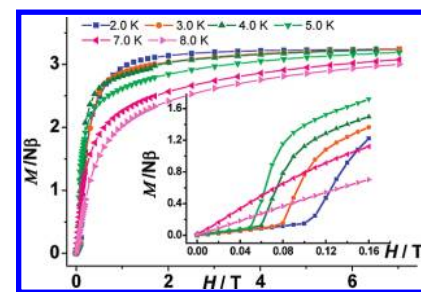

Figure 6. Plots of the magnetization at 2−8 K (the inset shows the detail in a low field (0 − 1.6 KOe) at 2−8 K).

$J = +41.7$ cm^{-1}, $zJ' = -0.26$ cm^{-1}, g = 2.06, and the agreement factor R (defined as $\sum[(\chi_M T)_{calc} - (\chi_M T)_{obs}]^2/\sum[(\chi_M T)_{obs}]^2) = 6.2 \times 10^{-5}$. The J value confirms the strong ferromagnetic interactions between the Cu^{II} ions through the double $\mu_{1,1}$-N_3 bridges in this uniform linear 1D array, and the value of zJ' imply that the totally weak interchain antiferromagnetic interactions may result from the cooperative exchange by the μ_3-N_3^- anion and interlayer antiferromagnetic coupling mediated by hydrogen bonding as well as dipole−dipole interactions, etc. To our knowledge, such structures containing linear 1D chains based on pentacoordinated copper(II) and singly doubled $\mu_{1,1}$-N_3 azido bridges are very rare, only three complexes have been characterized by both single-crystal X-ray diffraction and magnetic analyses. One is {[Pr$_4$N]$_2$[Cu$_3(\mu_{1,1}$-$N_3)_4(N_3)_4$]}$_n$ in which symmetry-related [Cu$_3(N_3)_8$]$^{2-}$ moieties are doubly $\mu_{1,1}$-azido bridged to form unprecedented infinite zigzag chains parallel to the crystallographic a-axis, for which the fitted g and J values is g = 2.25, $J = 7.0$ cm^{-1}.[10b] Another two complexes are homochiral 2D brick-wall complexes with only end-on azido bridges, [Cu$_3$((R)-phea)$_2$(N$_3$)$_6$]$_n$ and [Cu$_3$((S)-phea)$_2$-(N$_3$)$_6$]$_n$ (phea = 1-phenylethylamine), the fitted parameters refer to the intra-Cu(II)-azido chains ($J = 15.27$ cm^{-1}, g = 2.06).[20a] It is noted that the ferromagnetic interactions through the double $\mu_{1,1}$-N_3 azido

Table 1. Selected Structural and Magnetic Parameters for Singly Double $\mu_{1,1}$-N$_3$ Bridging of Main Cu(II) Based Complexes[a]

compound	Cu–Cu/Å	Cu–N–Cu/°	τ	J/cm^{-1}	ref
[Cu$_3$((R)-phea)$_2$(N$_3$)$_6$]$_n$	3.038, 3.015	96.3–101.8	0.07	15.3	20a
{[Pr$_4$N]$_2$[Cu$_3$($\mu_{1,1}$-N$_3$)$_4$(N$_3$)$_4$]}$_n$	3.178, 3.176	94.7–104.0	0.21	7.0	10b
[Cu($\mu_{1,1}$-N$_3$)$_2$(H$_2$O)]$_n$[CuL$_2$]	3.058, 3.065	99.9, 98.6	0.05	41.7	this work

[a] phea = 1-phenylethylamine; 2,2′-tpcb = rctt-tetrakis(2-pyridyl)cyclobutane; τ refers to Cu(II) centers of distortion index for double $\mu_{1,1}$-N$_3$ bridging chains in compound.

Table 2. Basical Summary of Cu(II) Based Metamagnet[a]

compound	D-	T (K)	H_c /Oe (T = 2 K)	ref
Cu$_5$(N$_3$)$_{10}$(en)$_2$	3D		8000	5a
Cu$_3$(N$_3$)$_6$(DMF)$_2$	2D		27000	6a
Cu(INO)(N$_3$)(H$_2$O)$_{0.5}$	3D	2.5	1000	6b
Cu(NNO)(N$_3$)(H$_2$O)$_{0.5}$	2D	3.5	3000	6b
CuL^{Et}	2D	4.5	$H_\perp$ = 1390	6c
			$H_\parallel$ = 420	
[NH$_3$(CH$_2$)$_3$NH$_3$]Cu$_3$(hedp)$_2$·3.5H$_2$O	2D		185	6d
[NH$_3$(CH$_2$)$_4$NH$_3$]Cu$_3$(hedp)$_2$·2H$_2$O	2D		48	6d
Cu$_4$[CH$_3$C(OH)(PO$_3$)$_2$]$_2$(C$_4$H$_4$N$_2$)(H$_2$O)$_4$	3D		2000–3000	6e
[Cu(mal)(0.5pyz)]·H$_2$O	3D	3.2	30000 (T = 1.8 K)	6f
Cu$_2$(N$_3$)$_2$(NO$_3$)$_2$(Me$_3$NCH$_2$CO$_2$)$_2$	1D	4.2	3500	6g
[Cu($\mu_{1,1}$-N$_3$)$_2$(H$_2$O)]$_n$[CuL$_2$]	2D		1200	this work

[a] L^{Et} = bis[4-(2-oxido-1-butenyl)-2,2,5,5-tetramethylimidazolidine-1-oxyl]; INO = isonicotinate N-oxide; NNO = nicotinate N-oxide; en = ethylenediamine; hedp = 1-hydroxyethylidenediphosphonate; mal = malonate dianion, pyz = pyrazine.

ligands in complex **1** are rather strong, compared with above three compounds. We attempted to explain this result in terms of the distortion index τ of the copper(II) center (Table 1). As can be seen, the coordination geometry of the metal ions for 1D chains in complex **1** shows the least distortion (τ = 0.05), and we have described it as a slightly distorted square pyramid. As the Cu–N–Cu angles (94.7–104.1°) for all these complexes are smaller than 108°,[21] the magnetic interactions between Cu(II) ions result in ferromagnetic, and a good coplanar linear structure for compound **1** leads to stronger F coupling (J increases) than others.

Notably, the bulky magnetic behavior of **1** is similar to that of the 2D coordination polymer [Cu$_3$(N$_3$)$_6$(DMF)$_2$]$_n$ with μ-1,1,1 and μ-1,1,3 azido anions, in which the ferromagnetic chains undergo antiferromagnetic coupling (Table 2), leading to a metamagnetic spin-flop transition under 2.7 T at 2 K.[6a] In contrast, for 3D complexes [Cu$_6$(N$_3$)$_{12}$(N-Eten)$_2$]$_n$ and {[Cu$_9$(N$_3$)$_{18}$(1,2-pn)$_4$]·H$_2$O}$_n$ with both μ-1,1,1 and μ-1,1,3 azide bridges, as well as 2D complexes [Cu(dacy)(N$_3$)$_2$]$_n$ and [Cu$_2$(me$_2$tn)$_2$(N$_3$)$_4$]$_n$ with μ-1,1, μ-1,3 and μ-1,1,3 azide bridges, only ferromagnetic ordering is observed.[20] Complex **1** also shows different magnetic behaviors in comparison with those of the other known examples for Cu-based metamagnets (Table 2). For example, the 2D or 3D Cu(II)-based coordination polymers in which the 3-fold mixed-bridged N$_3$/COO chains are further linked by the pyridyl N-oxide group show the metamagnetic transition of 3.0 and 1.0 kOe at 3.5 K, respectively;[6b] a layered polymeric copper(II) metamagnet with 3-imidazoline nitroxide has the transition critical field of 440 Oe;[6c] the metamagnetic copper(II) diphosphonates with layered or pillared-layer structures have the critical field of 48 Oe, 185 Oe, or 2–3 KOe, at which the antiferromagnetic ground-state is changed to a ferrimagnetic state at about 2 K;[6d,6e] two 2D metamagnet assembled by cyano-bridged Cu(II)–W(V) bimetallic system with the critical magnetic field of the spin-flip transition (220 Oe and 3.2 kOe).[22] Apparently, different types of homo- or heterospin systems and strong/weak exchange approaches result in the distinct efficiency of magnetic interactions and critical magnetic fields in the bulky metamagnetic materials.

In summary, a possible approach to the stepwise synthesis of a network-based copper(II) hybrid material with typical metamagnetic behavior is developed. The mutual stabilization of the 0D and 1D motifs in the unusual crystalline lattice of **1** is achieved by both coordination and supramolecular interactions. As a consequence, this material represents a unique copper(II)-based homospin metamagnet. These results not only provide the first example of microwave-assisted stepwise hydrothermal synthesis of organic–inorganic hybrids, but also open up a new route to the rational design of predictable magnetic networks.

Supporting Information Available: The figure for molecular packing, including synthetic methods, crystallography, including $1/\chi_m$ vs T plot, ZFC and FC plot, M vs H plot for **1**. Tables of Crystallographic Data and CIF files for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Synthesis: The starting mononuclear precursor of $[Cu(L)_2-(H_2O)] \cdot 3H_2O$ ($1'$) was synthesized by reacting 2-methylpyrazine-5-carboxylic acid (H**L**) with $CuCl_2$ in a basic solution, according to a literature method. Compound $1'$ was reacted further with an admixture of $Cu(NO_3)_2 \cdot 3H_2O$ and NaN_3 in a 1:2 molar ratio in an aqueous solution. The mixture was sealed in a 50-mL Teflon-lined, stainless-steel Parr bomb under microwave irradiation using a WX-4000 microwave digestion system (commercially available,

T = 140 °C; power = 300 W; pressure = 2.2 atm) for 30 min. Blue-black block crystals of **1** were observed and picked out, washed with distilled water, and then dried in air (yield: 30%, based on Cu, see Scheme 1). Caution! Azide compounds are potentially explosive. Only a small amount of materials should be handled carefully. Elemental analysis (%) calcd (found) for **1** ($C_{12}H_{14}Cu_3N_{16}O_6$): C, 21.54 (21.80); H, 2.11(1.91); N, 33.50 (33.62). Selected IR data (cm^{-1}): 3420s, 2088vs, 2053vs, 1650vs, 1600 m, 1374 m, 1330 m, 1280 m, 1054 m, 826w, 565w.

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(16) Crystal data for $C_{12}H_{14}Cu_3N_{16}O_6$: formula wt. 669.04, triclinic space group $P\bar{1}$, a = 6.0838(5) Å, b = 10.1516(7) Å, c = 10.6888(9) Å, α = 111.677(7), β = 100.962(7), γ = 105.125(7), V = 561.19(9) Å^3, Z = 1, D_{calc} = 1.980 g cm^{-3}, T = 123(2) K. R_1 = 0.0360 for 2169 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0906 for 5029 unique reflections (R_{int} = 0.0453).

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