Polynuclear Complexes

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Two Molecular Tapes Consisting of Serial or Parallel Azido-Bridged Eight-Membered Copper Rings**

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The construction of low-dimensional coordination polymers has received intense attention for a long time because of their structural diversity and unusual properties as well as their magneto–structural correlations.[1] Among them, some one-dimensional (1D) expanded chains with exotic topologies have been reported, such as ladders,[2] ropes,[3] and cluster-based chains.[4] They provide an intermediate step from 1D chains towards 2D networks, thus potentially helping the magnetic behavior at the border of 1D to 2D systems to be understood. As a versatile bridging ligand, the azido ion could link two or more metal ions in various modes, for example, μ-1,1 (end-on (EO)), μ-1,3 (end-to-end (EE)), μ-1,1,1, μ-1,1,3, and so forth, thus giving rise to a variety of zero- to three-dimensional polynuclear complexes.[5–9] As far as 1D chains are concerned, many unusual alternating chains with different combinations of these modes have been obtained.[7,8]

However, the synthesis of 1D chains of increasing width is still a big challenge. In our opinion, utilizing the diverse coordination geometry of the copper ion and the versatile bridging modes of the azide moiety might be key to facing the challenge. From the viewpoint of magneto–structural correlation, the azido–copper system might be one of the most complicated systems because of the various bridging modes of the azido ion and the Jahn–Teller effect of the copper ion in an

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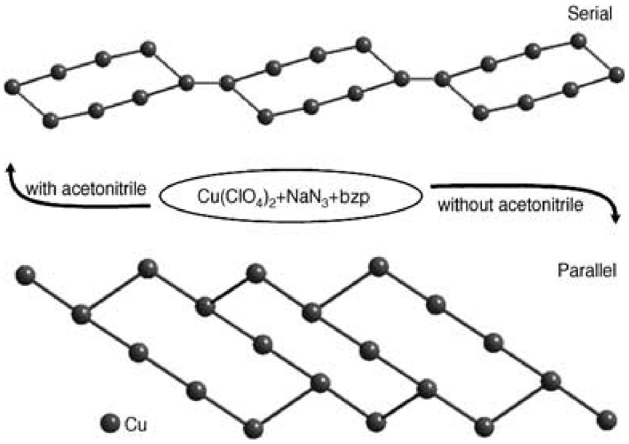
elongated octahedral or square-pyramidal geometry. Although it has been well stated both theoretically and experimentally that the exchange is ferromagnetic (F) or antiferromagnetic (AF) depending on the angle of Cu-N-Cu for the EO mode,[10] the correlation seems to be open ended for continuous exceptions.[11–12] In addition, to obtain an isolated 1D magnetic chain, a blocking coligand with stereochemical character, as well as an effective bridging ligand, is often needed to reduce the structural dimension and decrease the intermolecular interactions.

2-Benzoylpyridyl (bzp) has been used as a terminal/convergent coligand to form a 1D azido–manganese chain with interchain Mn⋯Mn distances of 10 Å.[13] We employed this coligand in an azido–copper system on the basis of these considerations and obtained an exotic 1D molecular tape, $[Cu_4(N_3)_8(CH_3CN)_3(bzp)_2]_n$ (**1**), with serial-connected cyclic azido-bridged eight-membered copper rings from the reaction solution of methanol/acetonitrile. Noticing that coordinated acetonitrile molecules might prevent further expansion of the tape, we changed the experimental conditions to 100% methanol as the solvent. Fortunately, we obtained another more interesting molecular tape, $[Cu_5(N_3)_{10}(bzp)_2]_n$ (**2**), with parallel eight-membered copper rings (Scheme 1). Herein, we report the synthesis, structure,[14] and magneto–structural correlations of these copper rings.



Scheme 1. Formation of molecular tapes **1** and **2**.

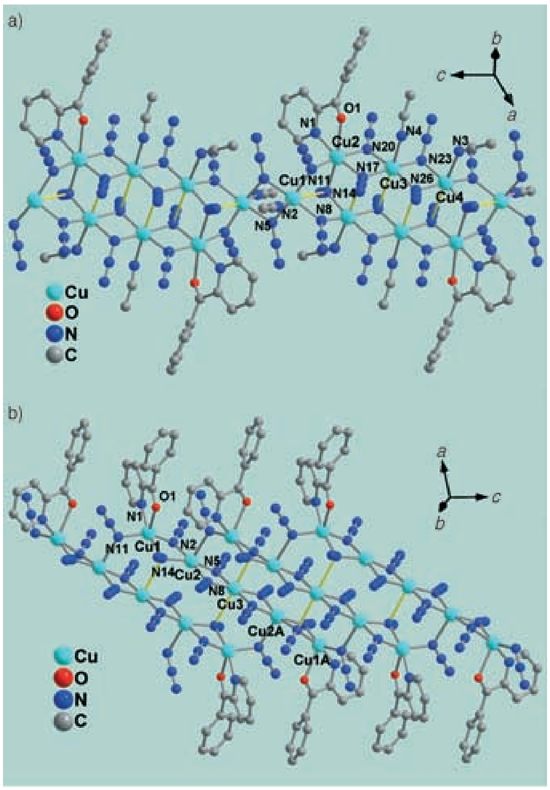


Figure 1. a) The ball and stick structure of the tape **1** with serial cyclic azido-bridged octanuclear copper clusters along the *c* axis (the yellow bonds are approximately 2.8 Å). b) The ball and stick structure of the tape **2** with the parallel linear azido-bridged pentanuclear copper units along the *c* axis (the yellow bonds are longer than 2.65 Å).

The single-crystal X-ray determination revealed that **1** consists of neutral 1D azido–copper chains with serial octanuclear repeating units (Figure 1a). There are four crystallographically independent Cu^{II} ions, with each assuming an elongated octahedral geometry; eight nonequivalent azido ligands, five (N5, N8, N11, N20, and N23) which adopt the EO bridging mode and the other three (N14, N17, and N26) which adopt the μ-1,1,1 mode; and three terminal acetonitrile molecules (N2, N3, and N4). For the Cu2 center, three azido atoms (N11, N17, and N20) and one pyridine nitrogen atom (N1) from the bzp ligand are in the basal sites, whereas the oxygen atom (O1) of the bzp ligand and one μ-1,1,1-azido ion are in the apical positions (Cu2–O1: 2.442 Å, Cu2–N14: 2.400 Å). The environment around the other three Cu^{II} ions are similar, with the nonequivalent apical positions occupied by one acetonitrile molecule ($Cu–N_{CH_3CN}$: 2.38–2.43 Å) and one μ-1,1,1-azido ion ($Cu–N_{azido}$: 2.71–2.82 Å) and the basal sites furnished by four azido ions ($Cu–N_{azido}$: 1.98–2.03 Å), thus the basal bonds are significantly shorter than the axial ones. Here, the distortion of the basal planes of the octahedral or square-pyramidal Cu^{II} ions could be described by a geometrical parameter τ in accord with the method of Addison et al. with $\tau = |\beta - \alpha|/60$, in which β and α are the bond angles that involve *trans* donor atoms in the basal plane.[15] All the τ values are around 0.05 for the Cu^{II} ions. The Cu-N-Cu angles vary from 82.85 to 102.74°, except for Cu1-N11-Cu2 and Cu1-N8-Cu4A which are 116.78 and 116.38°, respectively, and the dihedral angles ϕ between the basal planes of Cu1 and Cu2, Cu2 and Cu3, Cu3 and Cu4, and Cu4 and Cu1A are 68.9, 1.9, 6.9, and 72.8°, respectively. Thus, a unique centrosymmetric cyclic azido-bridged eight-membered copper ring $[Cu_8(N_3)_{14}(CH_3CN)_6(bzp)_2]^{2+}$ is formed, within which the metal ions are bridged by eight EO azido groups outside, whereas each of the three closest copper ions are bridged by one asymmetric μ-1,1,1-azido ligand inside. The adjacent rings are further linked in a serial mode to an exotic 1D chain by double EO bridges along the *c* axis. The chains of **1** are well isolated as the shortest Cu⋯Cu interchain distance is 8.3 Å, which is between the Cu2 and Cu2 centers ($-x+1$, $-y+1$, $-z+2$; see the Supporting Information).

The structure of **2** reveals a more interesting neutral azido–copper tape. There are three crystallographically independent Cu^{II} ions (Cu1, Cu2, and Cu3) and five nonequivalent azido ligands, which include three basal–basal EO azido (N2, N5, and N8) ligands, one basal–apical EO azido (N11) ligand, and one asymmetric μ-1,1,1-azido (N14) ligand (Figure 1 b). Both the Cu1 and Cu2 ions are five-coordinate with distorted square-pyramidal geometry (4 + 1): For the Cu1 center, three azido nitrogen atoms (N11, N2, and N14) and one pyridine nitrogen atom (N1) of the bzp ligand occupy the basal sites, thus leading to significantly shorter Cu–N bond lengths (1.89–1.92 Å), and the oxygen atom of the bzp ligand occupies the apical position (Cu1–O1: 2.27 Å). For the Cu2 center, only the azido ions are involved in the coordination, with the N11A atom at the apical position (Cu2–N11A: 2.275 Å). The values of τ are 0.28 and 0.18 for the Cu1 and Cu2 centers, respectively. The Cu3 ion ($\tau = 0$) lies in the symmetric center with an elongated octahedral geometry furnished by six azido ions, and the apical sites are occupied by two μ-1,1,1-azido (N14) atoms (Cu–N: 2.683 Å, which is much longer than the basal bonds as well as the apical bonds of the square-pyramidal Cu ions). Thus, the five copper ions (Cu1, Cu2, Cu3, Cu2A, and Cu1A) are bridged by double basal–basal EO azides to form a linear unit, in which the dihedral angles ϕ are 25.4° for the Cu1 and Cu2 centers and 5.8° for the Cu2 and Cu3 centers, and the bridge angles are 107.0° (∡ Cu1-N2-Cu2), 104.5° (∡ Cu1-N14-Cu2), and 107.7° (∡ Cu2-N5/N8-Cu3). The intraunit metal distances are Cu1···Cu2: 3.05 Å and Cu2···Cu3: 3.07 Å. The parallel neighboring units are further connected to a tape along the *c* axis through two basal–apical EO azido bridges (∡ Cu1-N11-Cu2B: 118°) and two asymmetric μ-1,1,1-azido bridges with an inter-unit metal distance of Cu1···Cu2B: 3.59 Å. The tapes are well isolated, with the shortest Cu···Cu intertape distance of 8.13 Å occurring between the Cu1 and Cu2 centers ($2-x$, $y-0.5$, $0.5-z$; see the Supporting Information). It is of note that if the weak Cu3–N_{azido} bonds (the yellow bonds in Figure 1 b) are omitted, the tape can also be viewed as a 1D chain that consists of parallel eight-membered copper rings (Scheme 1).

The magnetic susceptibilities of **1** and **2** (2–300 K) were measured at 1 kOe on a Quantum Design MPMS XL-5 SQUID system (Figure 2). For **1**, the $\chi_M T$ value per {Cu$_4$} unit increases gradually on cooling, thus suggesting an overall ferromagnetic coupling between the adjacent Cu^{II} ions, and there is an decrease in $\chi_M T$ below 4 K that may be because of an interchain AF and/or a zero-field splitting (ZFS) effect. The data above 70 K fit well with the Curie–Weiss law ($\chi_M = C/(T-\theta)$), thus giving $C = 1.79\,\mathrm{cm^3\,mol^{-1}\,K}$ (which corresponds to four uncoupled Cu^{II} ions with $g = 2.18$) and $\theta = 22.5$ K. No long-range ordering was observed above 1.9 K from the magnetization–temperature (*M–T*) curve at 20 Oe and *ac* susceptibilities versus the *T* curves (see the Supporting Information). The observed magnetization curve at 1.9 K is above the calculated Brillouin function for the sum of four isolated Cu^{II} ions ($S = 1/2$) below 50 kOe, thus confirming further the ferromagnetic coupling between the copper ions (see the Supporting Information).

For **2**, the $\chi_M T$ value of 2.2 cm^3 mol^{-1} K at 300 K per {Cu$_5$} unit decreases gradually on lowering the temperature and reaches a plateau at 1.5 cm^3 mol^{-1} K at 10–20 K (Figure 2 b), which is close to the $S = 3/2$ state (it was expected that $\chi_M T =$ 1.875 cm^3 mol^{-1} K at this point; however, the observed value is lower than the expected one, probably as a result of interpentanuclear AF interactions). The $\chi_M T$ value then decreases sharply, possibly because of the interpentanuclear interactions, and/or interchain AF interactions, and/or the ZFS effect as the field-saturation effect has been excluded by the similar decrease found in the $\chi_M T$–T curve at the fairly low field of 20 Oe (see the Supporting Information). Fitting the data above 100 K with the Curie–Weiss law gives $C = 2.26\,\mathrm{cm^3\,mol^{-1}\,K}$ (which corresponds to five independent spin-only Cu^{II} ions with $g = 2.19$) and a negative θ value of −12 K, thus indicating a net AF coupling among the metal ions. The magnetization value of 2.6 $N\beta$ per {Cu$_5$} unit at 50 kOe and 1.9 K, which is close to and slightly lower than the expected value of 2.9 $N\beta$ from the Brillouin function for a $S = 3/2$ system with $g = 2$, also implies a ferrimagnetic-like state in which $S = 3/2$, thus further suggesting the coexistence of antiferromagnetic and ferromagnetic couplings within the pentanuclear subunit. The AF interaction between the subunits was estimated to be −2.4 K by fitting magnetization–magnetic field (*M–H*) data by using a modified Brillouin function (see the Supporting Information).

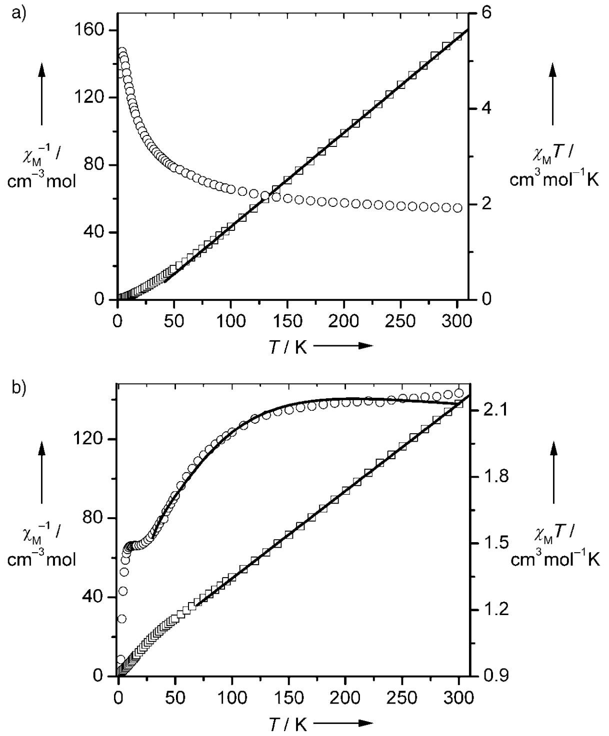


Figure 2. $\chi_M T$ and $1/\chi_M$ versus T in an applied field of 1 kOe for a) **1** and b) **2**. The lines are the best fits to the Curie–Weiss law and are an approximate uniform-chain model.

The magnetic behaviors of **1** and **2** can be rationalized on the basis of their structures. The EO bridges in the azido–copper system could be further divided into two types: 1) basal–basal bridges, in which the azido bridges are involved in two basal planes of Cu^{II} ions; 2) asymmetric basal–apical bridges, in which the azido group is located at the apical position of one of the Cu^{II} ions and the basal position of the other. It has been well documented that the exchange is F or

AF depending on the Cu-N-Cu angle for the basal–basal bridges (the calculated critical angle is 104° and experimentally derived angle is 108°)[10] and that the interaction through the basal–apical bridges is either negligible or weakly F/AF depending on the distortion of the basal planes of the Cu^{II} ions.[12] Taking into account the structure of **1**, interaction through the basal–apical bridges (between the $\{Cu_4\}$ units) is negligible because of very small distortions ($\tau \approx 0.05$). Figure 3 shows the resulting magnetic chain of **1,** in which the bridge angles are in the range 98.8–102.7°, except for the ∡ Cu1-N11-Cu2 and ∡ Cu1-N8-Cu4A angles of 116.5° which are anticipated to transmit strong AF coupling. Surprisingly, our magnetic measurements suggest that all the copper ions are F. To understand the unusual F interaction through the Cu1-N11-Cu2 bridges, preliminary theoretical studies were performed for the Cu1–Cu2 "dimer" model **1** formed from **1** (see the Supporting Information) by using the broken-symmetry approach under a DFT framework (DFT-BS).[16,17] The calculated results show that the "local magnetic orbitals" are mainly located at paramagnetic centers (Cu1 and Cu2); describe the distribution of the active spin electrons at each local magnetic center, that is to say, are beside the Cu1 and Cu2 centers, which also contain possible components of bridging and/or terminal ligands; and show that the $d_{x^2-y^2}$ orbitals occupied by nonpaired electrons in the Cu1 and Cu2 ions are located at the basal planes of the Cu1 and Cu2 centers. From the point of view of the molecular orbital theory, the two local magnetic orbitals on the Cu1 and Cu2 ions further constitute the singly occupied molecular orbitals in the triplet state (Figure 4). It is worth noting that the Cu1-N11-Cu2 bridge is different from other usual basal–basal EO bridges because of a large dihedral angle of 68.9° between the basal planes of the Cu1 and Cu2 centers, thus leading no doubt to a small overlap integral (calculated value of 0.0263) between the two local magnetic orbitals on the Cu1 and Cu2 centers. On the basis of the relationship[18] between the exchange constant J and the overlap integral S_{ab} between the local magnetic orbitals of a and b, $J = J_F + J_{AF} = 2K - US_{ab}^2$, in which K is the ferromagnetic contribution and U is the charge-transfer energy difference between the covalent and the ionic configurations, the small overlap integral should be responsible for the ferromagnetic interaction between the Cu1 and Cu2 centers. Additionally, we obtained the calculated exchange constant $J = 28.6\,cm^{-1} (H = -2JS_1S_2)$, which accounts just for the experimentally ferromagnetic interaction, by using the DFT-BS method.

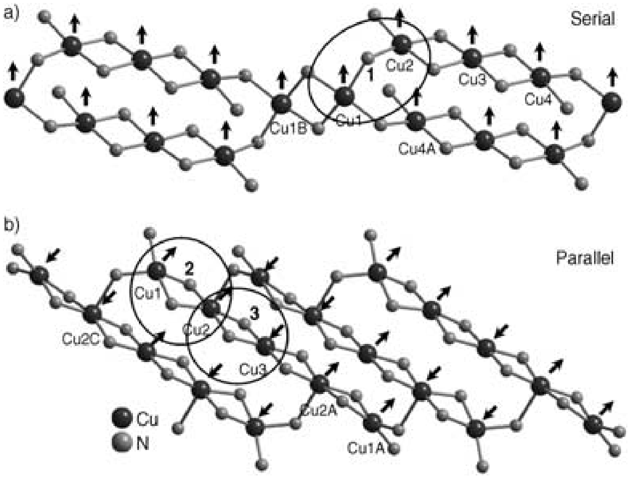


Figure 3. The magnetic chains of a) **1** and b) **2**.

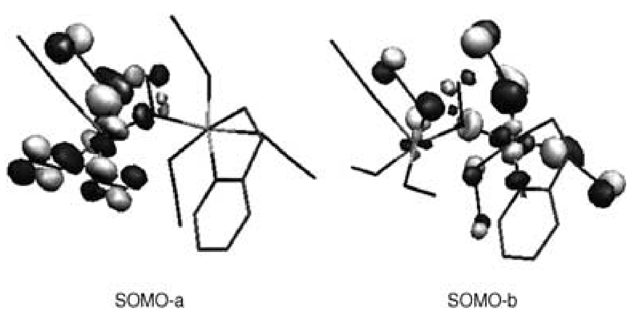


Figure 4. Singly occupied molecular orbitals of model **1** in the triplet state.

Figure 3b shows the structure of the magnetic chain of **2**, which is based on the following rational considerations: 1) interactions through the basal–apical bridges that occupy the apical positions of the Cu3 ions (the yellow bonds in Figure 1b) can be safely omitted; 2) the coupling through the Cu1-N11-Cu2C bridges between the adjacent pentanuclear units should be considered as J_1 because the distortion of the basal plane of the Cu1 and Cu2 ions cannot be considered as being small ($\tau \approx 0.18$–0.28); 3) J_2 and J_3 are used to calculate the magnetic exchange interactions for Cu1···Cu2 and Cu2···Cu3, respectively. On the basis of an approximate model,[19] **2** can be treated as a uniform chain with linear pentanuclear $\{Cu_5\}$ as a subunit, for which $H = -2J_2(S_{Cu1}S_{Cu2} + S_{Cu1A}S_{Cu2A}) - 2J_3(S_{Cu2}S_{Cu3} + S_{Cu3}S_{Cu2A})$ (for $\{Cu_5\}$); $H = -2J_1 \Sigma S_{p,i} S_{p,i+1}$ (S_p for $\{Cu_5\}$ as a classical system). Fixing $g = 2.19$, the best fitting of the data at 25–300 K gives $J_1 = -1.5$, $J_2 = 112$, and $J_3 = -29\,cm^{-1}$, with $R = 8 \times 10^{-5}$ ($R = \Sigma[(\chi_M T)_{obsd} - (\chi_M T)_{calcd}]^2 / \Sigma(\chi_M T)^2_{obs}$). The negative J_1 value of $-1.5\,cm^{-1}$, which indicates AF coupling between the pentanuclear units, is consistent with the estimated value of -2.4 K from the M–H fitting (see the Supporting Information). The theoretical calculations of the "dimer" models of Cu1–Cu2 and Cu2–Cu3 in **2** are also performed by using the DFT-BS approach (see the Supporting Information). The calculated results of $J_2 = 113$ and $J_3 = -22\,cm^{-1}$ reproduced the experimentally derived F and AF characteristics well for Cu1–Cu2 and Cu2–Cu3, respectively. Further inspection of the calculated overlap integrals between the local magnetic orbitals $d_{x^2-y^2}$ on the Cu^{II} ions shows that the small overlap integral (0.0139) between the Cu1 and Cu2 centers and the larger overlap integral (0.136) between the Cu2 and Cu3 centers are responsible for these magnetic coupling characteristics. The large difference might come from three possibilities: 1) using **1**, which has a large ϕ value, as a ferromagnetic reference, the ϕ value of 25.4° between the Cu1 and Cu2 centers in **2**, which cannot be considered as small, might also contribute to the ferromagnetic coupling; 2) the large distortion ($\tau = 0.28$ and 0.18 for Cu1 and Cu2, respectively) also could cause a small overlap between the local magnetic orbitals on the Cu1 and Cu2 centers; 3) as the magnetic coupling J often has a strong dependence on the Cu-N-Cu angle θ and as $2J = 4440–41.94\ \theta(\mathrm{cm}^{-1})$,[10d] it is evident that the small angles of Cu1-N-Cu2 (104.5 and 107°) would transfer a ferromagnetic interaction more readily than Cu2-N-Cu3 (107.7 and 107.7°). However, it is unclear which is the dominant reason at the present stage.

In summary, we have obtained two exotic 1D molecular tapes with serial and parallel cyclic azido-bridged eight-membered copper rings $[\mathrm{Cu_4(N_3)_8(CH_3CN)_3(bzp)_2}]_n$ (**1**) and $[\mathrm{Cu_5(N_3)_{10}(bzp)_2}]_n$ (**2**) in solution with methanol, either with or without the addition of acetonitrile. It is of note that the EO bridge in **1**, in which the Cu-N-Cu angle is 116° and $\phi = 68.9°$, is observed to transmit ferromagnetic interactions and that the central copper center of the linear pentanulear $\{\mathrm{C_5}\}$ unit in **2** is antiferromagnetically coupled with its neighboring Cu ions and has a ground state S of 3/2. The magneto–structural correlation for a basal–basal EO azido bridge in the azido–copper system is not only dependent on the Cu-N-Cu angle; therefore, more factors should be taken into account, such as the dihedral angle ϕ between the basal planes of the two bridged copper ions as well as the distortion from square-pyramidal to trigonal-bipyramidal geometry for the $\mathrm{Cu^{II}}$ ion.

Experimental Section

1: A solution of $\mathrm{Cu(ClO_4)_2{\cdot}6\,H_2O}$ (185 mg, 0.5 mmol) in acetonitrile (15 mL) was mixed with a solution of bzp (92 mg, 0.25 mmol) and $\mathrm{NaN_3}$ (65 mg, 1 mmol) in methanol (15 mL). The resulting solution was kept undisturbed at room temperature. Brown platelike single crystals of **1** were obtained after several days. Yield: 58 mg, 52 %. Elemental analysis (%) calcd for $\mathrm{C_{18}H_{18}Cu_4N_{28}O}$: C 24.11, H 2.02, N 43.74; found: C 23.73, H 2.14, N 43.14; IR: $\tilde{\nu} = 2046$, 2080, and 2089 (vs) for the azide group and 2262 and 2295 $\mathrm{cm^{-1}}$(w) for $\mathrm{CH_3CN}$.

2: A solution of $\mathrm{Cu(ClO_4)_2{\cdot}6\,H_2O}$ (185 mg, 0.5 mmol) in methanol (15 mL) was mixed with a solution of bzp (92 mg, 0.5 mmol) and $\mathrm{NaN_3}$ (45 mg, 0.7 mmol) in methanol (15 mL). The resulting solution was left at room temperature. Green blocklike single crystals were isolated and brown striplike single crystals of **2** were obtained after 2 weeks. Yield: 18 mg, 24 %. Elemental analysis (%) calcd for $\mathrm{C_{24}H_{18}Cu_5N_{32}O_2}$: C 26.10, H 1.64, N 40.59; found: C 26.54, H 1.91, N 40.15. IR $\tilde{\nu} = 2052$, 2076, 2095, and 2119 $\mathrm{cm^{-1}}$ (v s) for the azide group.

All theoretical calculations were performed by the Amsterdam Density Functional (ADF) program, version 2004.01.[16] The VWN local density approximation,[20] and Operdew nonlocal density corrections[21] are used. The calculations on the magnetic-exchange constant J are based on the broken-symmetry approach developed by Noodleman.[17] The details of the method used for the calculation are described elsewhere.[22] The geometry of the dimer models **1**–**3** was adapted according to the experimentally crystal structure data, in which the bzp ligand was simplified (see the Supporting Information).

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[14] Crystal data for **1**: $C_{18}H_{18}Cu_4N_{28}O$, $M_r = 896.76$, monoclinic, space group $P2_1/c$, $a = 11.8532(2)$, $b = 21.4355(4)$, $c = 14.2472(2)$ Å, $\beta = 113.7515(11)°$, $V = 3313.31(10)$ Å^3, $Z = 4$, ρcalcd = 1.798 g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(\mathrm{Mo_{K\alpha}}) = 2.598$ mm^{-1}, $F(000) = 1784$, GOF = 1.015. A total of 49774 reflections were collected and 7610 are unique ($R_{int} = 0.0759$). $R1$ and $wR2$ are 0.0381 and 0.0831, respectively, for 462 parameters and 7610 reflections ($I > 2\sigma(I)$). **2**: $C_{24}H_{18}Cu_5N_{32}O_2$, $M_r = 1104.40$, monoclinic, space group $C2/c$, $a = 22.9413(6)$, $b = 14.4026(4)$, $c = 10.7951(3)$ Å, $\beta = 97.2433(12)°$, $V = 3538.39(16)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.073$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu(\mathrm{Mo_{K\alpha}}) = 3.039$ mm^{-1}, $F(000) = 2188$, GOF = 0.861. A total of 36150 reflections were collected and 4062 are unique ($R_{int} = 0.1019$). *R1* and $wR2$ are 0.0336 and 0.0724, respectively, for 286 parameters and 4062 reflections ($I > 2\sigma(I)$). The data were collected on an Enraf-Nonius Kappa CCD with $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods and refined with full-matrix least-squares on F^2 by using the SHELX-97 program. All non-hydrogen atoms were refined anisotropically. CCDC-268022 (**1**) and -268023 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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