Toward Tuning the Bulk Magnetic Behaviors of Metal−Azido Materials by Organic Pillars

Pei-Pei Liu, Ai-Ling Cheng, Na Liu, Wei-Wei Sun, and En-Qing Gao*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, People's Republic of China

Received March 27, 2007
Revised Manuscript Received April 24, 2007

The study of molecular magnetic materials, in which paramagnetic centers (mostly transition metal ions) are linked into molecule-based aggregates by diamagnetic bridges that can efficiently mediate magnetic exchange, has evoked considerable interest in the past two decades.[1] In this context, the azido ion is among the most extensively studied bridge, and its abilities in bridging metal ions in various modes, propagating magnetic exchange of a different nature, and building extended networks (clusters or infinite polymers) with diverse topologies have been demonstrated by a plethora of studies.[2−4] The known infinite metal−azido networks are mostly one-dimensional (1D) and two-dimensional (2D) systems,[4,5] with only a few examples of three-dimensional (3D) networks.[6] For the 1D or 2D systems (chains or layers), the bulk magnetic properties depend strongly on the interchain or interlayer interactions, besides the intrachain or intralayer magnetic factors. Thus, a problem arises: how to control or tune the interchain/interlayer interactions to get materials with specific bulk magnetic properties? It is a very tough problem, because the interactions are related to the packing of the chains or layers, and the intermolecular forces that determine the packing are usually very weak, very subtle, and hence very difficult to control. A possible strategic solution is to cross-link the low-dimensional motifs into 3D networks with organic bridging ligands,[7,8] which, with specific geometric and electronic features, may act as the covalent regulators tuning the inter-motif packing and interactions. For this purpose, it is highly desirable to obtain a series of 3D networks in which the same low-dimensional azido-bridged motifs are linked by different organic linkers, and thus one can investigate the exclusive influence of the organic linkers on the inter-motif interactions and the bulk magnetic properties. This is a great synthetic challenge because the metal−azido motifs are very sensitive to coligands: even with very similar organic linkers, the motifs are different.[7a] On the other hand, the known examples of 3D networks built from azido-bridged chains or layers are still rare and mainly limited to Mn(II) compounds,[7] with much fewer species with Co(II),[8a−c] Fe(II),[8f] Cu(II),[8c−e] and Ni(II).[8c] For Cu(II), the construction of 3D networks is more challenging, because Cu(II) usually takes a lower coordination number (5 or even 4).

Here we report two novel 3D species with the pillared-layer structure, $[Cu_2(N_3)_4(btze)]_n$ (**1**) and $[Cu_2(N_3)_4(btzb)]_n$ (**2**) (btze = 1,2-bis(tetrazol-1-yl)ethane and btzb = 1,4-bis-(tetrazol-1-yl)butane), in which the same Cu(II)−azido 2D layers are pillared by two similar organic linkers of different length. The exclusive influence of the linker length on magnetic behaviors is thus revealed. Both compounds behave as metamagnets. The 2D layer, with an unprecedented metal−azido bridging topology, is built through symmetric μ-1,1 and asymmetric μ-1,1,3 azides, both of which propagate ferromagnetic interactions. The change in the linker length can effectively tune the interlayer antiferromagnetic interactions and hence the critical fields for the metamagnetic transitions.

The complexes were synthesized by diffusing an ethanol solution of $CuCl_2$ into the aqueous solution containing sodium azide and appropriate organic ligands (see Supporting Information). X-ray crystallographic analyses[9] revealed that both complexes are 3D coordination polymers, in which 2D inorganic layers of Cu(II) ions and azido ions are interlinked by organic ligands. The two complexes are isomorphous, and their layer structures are essentially identical, so only the structure of **1** is detailed as follows (Figure 1). Each Cu(II) ion in the complex assumes the axially elongated

---

(1) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Miller, J. S., Drilon, M., Eds. *Magnetism: Molecules to Materials*; Willey-VCH: Weinheim, 2002. (c) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed*. **2003**, *42*, 268.

(2) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, *193−195*, 1027 and references therein.

(3) (a) Escuer, A.; Aromi, G. *Eur. J. Inorg. Chem.* **2006**, 4721. (b) Zhang, Y.-Z.; Wernsdorfer, W.; Pan, F.; Wang, Z.-M.; Gao, S. *Chem. Commun.* **2006**, *31*, 3302.

(4) (a) Liu, X.-T.; Wang, X.-Y.; Zhang, W.-X.; Cui, P.; Gao, S. *Adv. Mater.* **2006**, *18*, 285. (b) Liu, F.-C.; Zeng, Y.-F.; Zhao, J.-P.; Hu, B.-W.; Bu, X.-H.; Ribas, J.; Cano, J. *Inorg. Chem.* **2007**, *46*, 1520. (c) Gao, E.-Q.; Bai, S.-Q.; Yue, Y.-F.; Wang, Z.-M.; Yan, C.-H. *Inorg. Chem*. **2003**, *42*, 3642. (d) Gao, E.-Q.; Bai, S.-Q.; Wang, C.-F.; Yue, Y.-F.; He, Z.; Yan, C.-H. *Inorg. Chem*. **2003**, *42*, 8456.

(5) (a) You, Y. S.; Yoon, J. H.; Kim, H. C.; Hong, C. S. *Chem. Commun.* **2005**, *32*, 4116. (b) Escuer, A.; Mautner, F. A.; Goher, M. A. S.; Abu-Youssef, M. A. M.; Vicente, R. *Chem. Commun.* **2005**, *5*, 605. (c) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *Chem. Mater.* **2004**, 1590. (d) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 1419.

(6) (a) Goher, M. A. S.; Cano, J.; Journaux, Y.; Abu-Youssef, M. A. M.; Mautner, F. A.; Escuer, A.; Vicente, R. *Chem.−Eur. J.* **2000**, *6*, 778. (b) Mautner, F. A.; Cortés, R.; Lezama, L.; Rojo, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 78. (c) Mautner, F. A.; Hanna, S.; Cortés, R.; Lezama, L.; Barandika, M. G.; Rojo, T. *Inorg. Chem.* **1999**, *38*, 4647. (d) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *Inorg. Chem.* **1996**, *35*, 6386.

(7) (a) Gao, E.-Q.; Cheng, A.-L.; Xu, Y.-X.; He, M.-Y.; Yan, C.-H. *Inorg. Chem.* **2005**, *44*, 8822. (b) Gao, E.-Q.; Wang, Z.-M.; Yan, C.-H. *Chem. Commun.* **2003**, 1748. (c) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A.; Abu-Youssef, M. A. M. *Chem. Commun.* **2002**, 64. (d) Han, S.; Manson, J. L.; Kim, J.; Miller, J. S. *Inorg. Chem.* **2000**, *39*, 4182. (e) Ma, B.-Q.; Sun, H.-L.; Gao, S.; Su, G. *Chem. Mater.* **2001**, *13*, 1946. (f) Liu, C.-M.; Gao, S.; Zhang, D.-Q.; Huang, Y.-H.; Xiong, R.-G.; Liu, Z.-L.; Jiang, F.-C.; Zhu, D.-B. *Angew. Chem., Int. Ed.* **2004**, *43*, 990.

(8) (a) Wang, X.-Y.; Wang, L.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2006**, *128*, 674. (b) Liu, F.-C.; Zeng, Y.-F.; Jiao, J.; Bu, X.-H.; Ribas, J.; Batten, S. R. *Inorg. Chem*. **2006**, *45*, 2776. (c) He, Z.; Wang, Z.-M.; Gao, S.; Yan, C.-H. *Inorg. Chem.* **2006**, *45*, 6694. (d) Zeng, Y.-F.; Liu, F.-C.; Zhao, J.-P.; Cai, S.; Bu, X.-H.; Ribas, J. *Chem. Commun.* **2006**, *21*, 2227. (e) Du, M.; Guo, Y.-M.; Chen, S.-T.; Bu, X.-H.; Batten, S. R.; Ribas, J. *Inorg. Chem.* **2004**, *43*, 1287. (f) Fu, A. H.; Huang, X. Y.; Li, J.; Yuen, T.; Lin, C. L. *Chem.−Eur. J.* **2002**, *8*, 2239.

10.1021/cm0708416 CCC: $37.00

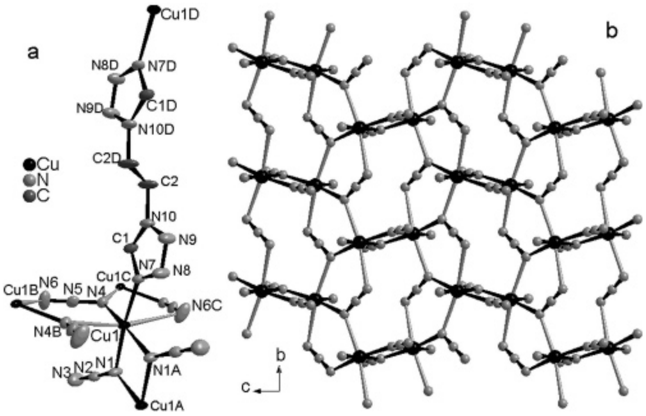

Figure 1. (a) Environments of the metal ions and the ligands in complex **1**. (b) The 2D Cu(II)−azido layer along the *bc* plane.

octahedral coordination geometry. The equatorial positions are occupied by three azido nitrogen atoms (N1, N1A, and N4) and one nitrogen atom from ligand btze (N7), with the Cu−N distances ranging from 1.992(2) Å to 2.007(1) Å. The axial positions are occupied by two azido nitrogen atoms (N4B and N6C), with the Cu−N distances [2.547(0) Å and 2.759(1) Å] being significantly longer than the equatorial ones. The azido ions adopt two kinds of bridging modes: μ-1,1 and μ-1,1,3. Two neighboring Cu(II) ions are doubly linked by two equivalent μ-1,1 azido bridges, which take the equatorial−equatorial (e−e) disposition with the bridging atoms (N1 and N1A) at the equatorial positions of both metal ions. In the resulting centrosymmetric binuclear unit, the Cu_2N_2 ring is strictly planar, with the Cu−N−Cu bridging angle and the Cu···Cu distance being 103.06(0)° and 3.131(2) Å, respectively. Each binuclear unit is connected to six neighbors through six μ-1,1,3 azido ions, generating a 2D Cu−azido layer parallel to the bc plane. Each μ-1,1,3 azido ion adopts an equatorial−axial−axial (e−a−a) disposition, that is, one terminal nitrogen (N4) occupies the equatorial position of a Cu ion but the axial position of the second Cu ion, with the other terminal nitrogen (N6) at the axial position of the third Cu ion. Two Cu ions from nearest binuclear units are doubly linked by an e−a single-atom bridge (Cu−N4−Cu, 135.8(1)°) and an e−a three-atom bridge (Cu−N−N−N−Cu torsion angle, 25.6(1)°) from different μ-1,1,3 azido ions, with Cu···Cu = 4.220(1) Å. The μ-1,1,3 azido ion also set up an a−a three-atom bridge between the next-nearest binuclear units, with Cu···Cu = 6.350(1) Å and Cu−N−N−N−Cu = 13.5(1)°. It is noted that the Cu(II)−azido lattice is distinct from other 2D metal−azido lattices reported in the literature. Most of the known lattices are supported by μ-1,3 and/or μ-1,1 azido bridges with different net topology, and lattices with only μ-1,1,3 azido bridges have also been reported.[5a]

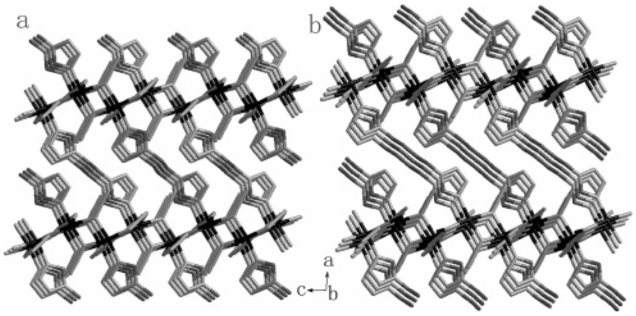

Figure 2. 3D networks of **1** (a) and **2** (b) viewed down the *b*-axis.

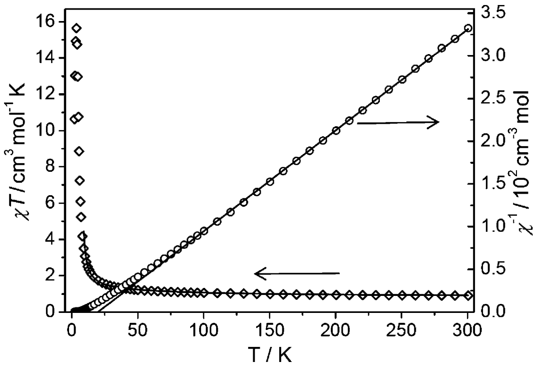

Figure 3. Temperature dependence of χ^{-1} and χT for complex **1**.

The 2D inorganic layers are pillared into a 3D inorganic−organic hybrid coordination network by the btze molecules connecting Cu(II) ions from neighboring layers (Figure 2a). The pillar ligand, with an inversion center at the midpoint, is slanted significantly with respect to the normal direction of the layers. Consequently, the Cu···Cu distance (11.693(1) Å) spanned by the ligand is significantly longer than the shortest interlayer Cu···Cu distance (9.988(5) Å). As expected, the replacement of btze by the longer btzb pillar significantly expands the separation between the metal−azido layers (Figure 2b): the Cu···Cu distance spanned by the ligand is increased to 14.041(1) Å, and the shortest interlayer Cu···Cu distance is increased to 11.726(5) Å.

The magnetic susceptibilities of compounds **1** and **2** were measured under 1 kOe in the temperature range of 2−300 K (Figure 3 for **1** and Figure S1, Supporting Information, for **2**). For **1**, the χT value per formula at 300 K is approximately 0.92 $cm^3\ mol^{-1}$ K. With the decrease of temperature, the χT value increases slowly, rises up quickly below 20 K, reaches a maximum of 15.64 $cm^3\ mol^{-1}$ K at 3.5 K, and then decreases sharply upon further cooling to 1.8 K. The χ^{-1} versus T plot above 70 K is linear, following the Curie−Weiss law with $C = 0.85$ $cm^3\ mol^{-1}$ K and $\theta = 19.9$ K. These features clearly indicate that ferromagnetic interactions between Cu ions are predominant throughout the layer. The abrupt drop in χT below 3.5 K may be due to the saturation effect rather than antiferromagnetic interactions (see below). The temperature-dependent behaviors of **2** are very similar, which is the reflection of the structural similarity of the metal−azido layers.

According to the layer structure, each Cu(II) is linked to five others through three different bridging moieties: the symmetric double e−e bridge consisting of two μ-1,1 azides, the double e−a bridge containing a single-atom linkage and

---

(9) Crystal data: **1**, $C_4H_6Cu_2N_{20}$, $M_r = 461.37$, monoclinic, space group $P2_1/c$, $a = 10.5567(18)$ Å, $b = 6.3046(11)$ Å, $c = 10.8182(18)$ Å, $\beta = 95.092(2)°$, $V = 717.2(2)$ Å^3, $Z = 2$, μ(Mo Kα) = 3.012 mm^{-1}, $\rho_{calcd} = 2.137$ g cm^{-3}, $T = 298$ K, $S = 1.073$, R1 = 0.0259 for 1397 reflections with $I > 2\sigma(I)$, and wR2 = 0.0658 for 1628 independent reflections; **2**, $C_6H_{10}Cu_2N_{20}$, $M_r = 489.42$, monoclinic, space group $P2_1/c$, $a = 11.859(2)$ Å, $b = 6.3786(11)$ Å, $c = 10.7701(18)$ Å, $\beta = 95.931(2)°$, $V = 810.3(2)$ Å^3, $Z = 2$, μ(Mo Kα) = 2.672 mm^{-1}, $\rho_{calcd} = 2.006$ g cm^{-3}, $T = 293$ K, $S = 1.049$, R1 = 0.0423 for 1550 reflections with $I > 2\sigma(I)$, and wR2 = 0.0976 for 1855 independent reflections.

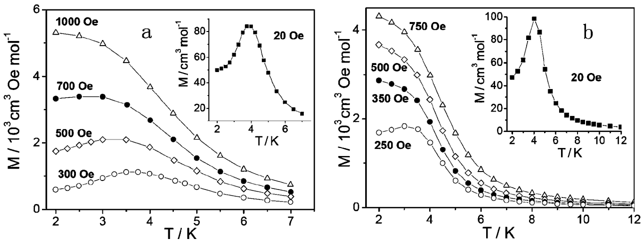

Figure 4. FC magnetization plots at different fields for **1** (a) and **2** (b).

a three-atom linkage from different *μ*-1,1,3 azides, and the single a−a bridge set up by the three-atom linkage of the *μ*-1,1,3 azide. Because the $d_{x^2-y^2}$-type magnetic orbital of Cu(II) is mainly delocalized over the equatorial plane, the exchange is propagated principally through the e−e bridge, the exchange through the e−a bridge is much weaker,[1a,4d] and that through the a−a bridge should be negligible. Accordingly, from the magnetic viewpoint, the layer consists of dicopper dimers with double e−e *μ*-1,1 bridges, which propagate strong ferromagnetic coupling, and each dimer is weakly and ferromagnetically coupled with four neighbors via double e−a bridges. Therefore, we used the well-known Bleaney−Bowers equation[10a] to evaluate the intradimer coupling (J) and the molecular-field approximation[10b] ($z = 4$) to account for the interdimer coupling (j). The simulations of the observed susceptibilities above 9 K led to $J = 71.3$ cm^{-1}, $j = 1.8$ cm^{-1}, and $g = 2.12$ for **1** and $J = 78.1$ cm^{-1}, $j = 1.7$ cm^{-1}, and $g = 2.12$ for **2**. The positive values of the interaction parameters support the ferromagnetic nature of the Cu−azido layers in **1** and **2**.

The temperature dependent behaviors were further investigated under different fields (Figure 4). The field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves at 20 Oe for each compound show no obvious differences, and for both compounds, the curves exhibit maximums around 4 K, suggesting the presence of interlayer antiferromagnetic interactions and the onset of long-range antiferromagnetic ordering below approximately 4 K. As the field is lifted, the maximums shift to lower temperature and disappeared above certain critical fields. These behaviors are typical of field-induced metamagnets, for which the disappearance of the maximums indicates that the interlayer antiferromagnetic interactions are overcome by the field. It is interesting to note that the critical field for **2** above which the maximum disappears is evidently lower than that for **1**. This observation can be rationally correlated to the structural difference of the two materials: the increased interlayer Cu···Cu separations in **2** dictate reduced interlayer antiferromagnetic interactions and hence a relatively lower magnetic field is sufficient to overcome the interactions.

The field dependent magnetizations were measured at 2 K (Figure 5). As the field is increased, the magnetizations for both compounds approach the saturation value (2.11 N*β* at 50 kOe) much more rapidly than expected for the $S = 1$ state (the ground state for a ferromagnetic dicopper(II) molecule). This confirms the ferromagnetic interactions in the compounds. The sigmoid shape of the magnetization curves under low field (Figure 5, inset) is typical of metamagnets: the slow increase of the magnetization in the very low field region is consistent with 3D antiferromagnetic ordering of the ferromagnetic layers, and the succeeding rapid rise indicates the onset of the field-induced spin-flop transitions. The critical fields, at which the $\partial M/\partial H$ derivatives reach maximums, are approximately 700 and 300 Oe, respectively. These results are in good agreement with those obtained from FC measurements. Loop measurements indicated very small hystereses for both compounds (Figure S2, Supporting Information).

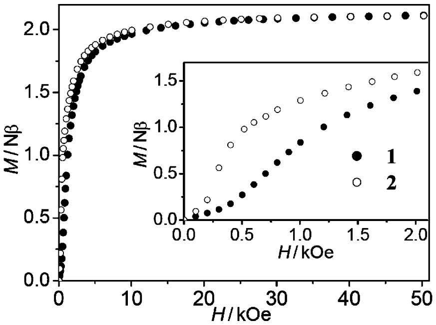

Figure 5. Field dependence of magnetization at 2 K for **1** and **2**. Inset: a blowup of the low-field region.

To summarize, we successfully obtained a novel type of 3D hybrid frameworks, in which the 2D Cu(II)−azido inorganic layers constructed via both *μ*-1,1 and *μ*-1,1,3 bridges are pillared by organic spacers. The 2D azido-bridged magnetic lattice is unprecedented, and the compounds represent the first examples of 3D molecular metamagnets built of ferromagnetic Cu(II)−azido layers. More remarkably, they offer us an uncommon opportunity to investigate the exclusive influence of the pillar length on bulk magnetic behaviors: the interlayer antiferromagnetic interactions and hence the critical fields for metamagnetic transitions can be effectively tuned by varying the pillar length. Further investigations along this line will help us to understand and control the magnetic interactions between low-dimensional motifs at the supramolecular level, contributing to the rational design of molecular magnets.

Acknowledgment. The authors thank NSFC (20571026 and 20490210), MOE (NCET-05-0425), and Shanghai "Shuguang" Project (04SG28) for the financial support.

Supporting Information Available: Experimental details, magnetic plots (PDF), and X-ray crystallographic information (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0708416

---

(10) (a) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Series A* **1952**, *214*, 451. (b) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.