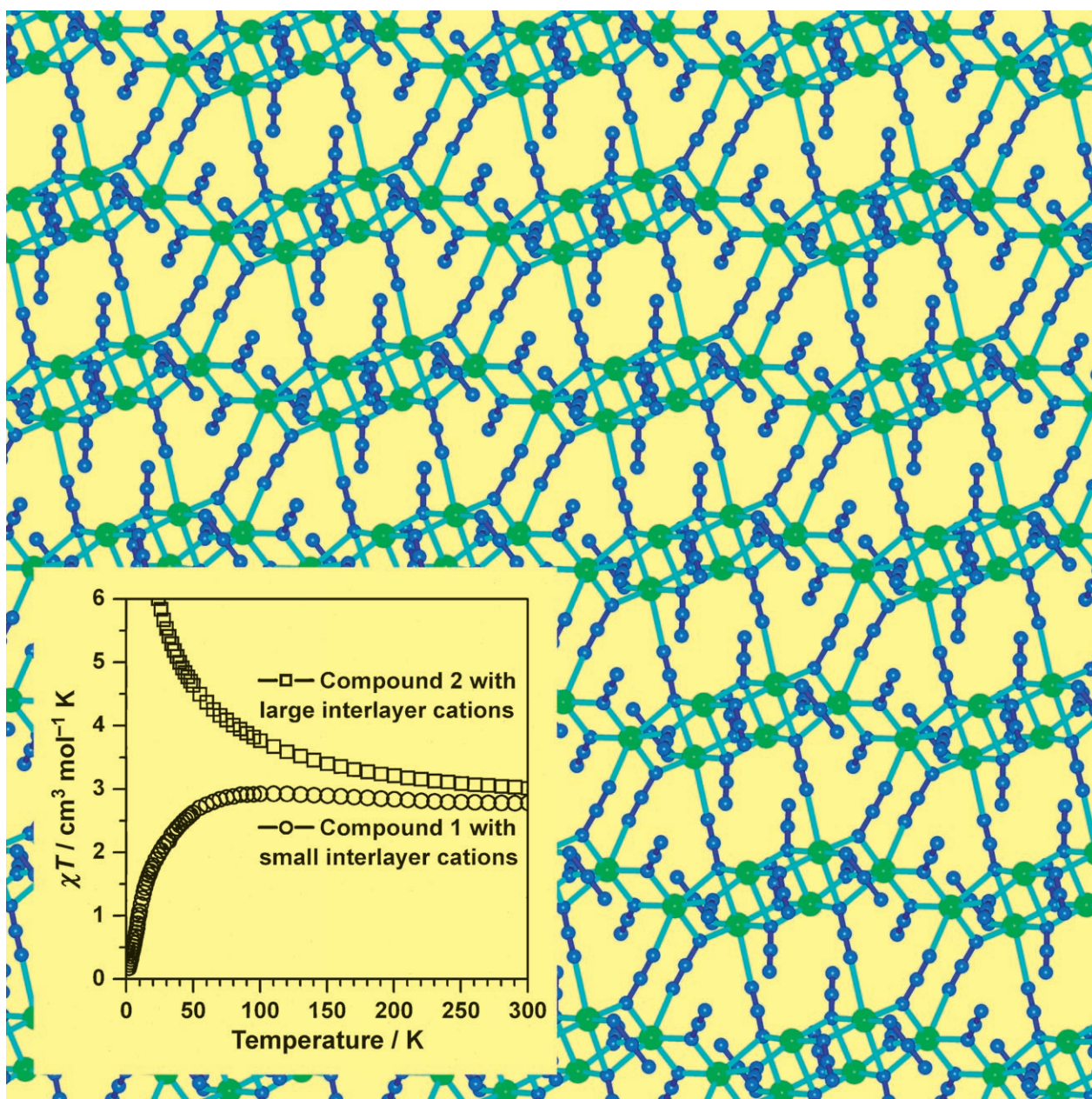# FULL PAPERS

Two Diammonium Copper Azides with Similar Layerlike Magnetic Substructures Made of Chains of Serially Connected Cu$_6$ Rings Show Cation-Modulated Magnetism

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Abstract: We present here the first examples of Cu–azide compounds synthesized by using protonated diamine ions as cationic templates: $(dmenH_2)$ $[Cu_6(N_3)_{14}]$ and $(trimenH_2)[Cu_6(N_3)_{14}]$ $(dmenH_2^{2+}$: N,N'-dimethylethylene-diammonium; $trimenH_2^{2+}$: N,N,N'-trimethylethylenediammonium). Both compounds possess a similar, rarely observed anionic Cu–azide layer, which consists of $[Cu_6(N_3)_{14}{}^{2-}]_n$ anionic chains linked by asymmetric end-to-end azido bridges. The chain, in turn, is made up of elongated Cu_6 rings, with double and single end-on azido linkages between the square-planar Cu^{2+} sites within the ring and double end-on azido bridges serially connecting the rings. The molecular geometry results in ferromagnetic interactions within the Cu–azide layer in both compounds. The interlayer separations are determined by the cations, with the shortest interlayer Cu···Cu separations being 8.016 Å for the $dmenH_2^{2+}$ compound and 9.106 Å for the $trimenH_2^{2+}$ compound. These different interlayer separations tune the magnetic properties of the two materials. The $dmenH_2^{2+}$ compound displays long-range antiferromagnetic ordering at low temperature and short-range ferromagnetic interaction at high temperature, while only short-range ferromagnetism was observed in the $trimenH_2^{2+}$ compound at 2–300 K.

Keywords: azides · copper · diammonium · magnetism · structure

Introduction

In the study of molecular-based magnetic materials, azido-bridged compounds have attracted great attention.[1–8] Possessing diverse coordination modes and being an efficient magnetic coupler, the azide anion is a versatile ligand in bridging different transition metals, generating rich and fascinating architectures ranging from discrete polynuclear species to extended networks with interesting magnetic properties. Azide can link metal ions in $\mu_{1,1}$ (end-on, EO), $\mu_{1,3}$ (end-to-end, EE), $\mu_{1,1,3}$, or other modes, and the magnetic exchange mediated through an azido bridge could exhibit ferromagnetism (FM) or antiferromagnetism (AF), depending on the bridging mode, bonding geometries, and the kind of metal ions.[2–4] For example, the azido bridge in the EO mode transmits FM for Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} in most cases,[1a,2a,3] while for Cu^{2+}, it depends on the bridging Cu-N-Cu angle as well as the dihedral angle between the two Cu basal planes.[2a,4] In general, the EE-azido bridge would transmit AF, but an increasing number of exceptions (say,

FM) have been reported recently,[5,6] especially for Cu–azides with asymmetric EE-azido bridges.[2b,6]

Besides the binary azides,[7] metal–azide compounds could be roughly divided into two classes, 1) those with coligands and 2) those with anionic metal–azide substructures induced by cations or cationic templates (sometimes small coligands like H_2O are involved). The first class includes many compounds, which extend from discrete molecular species (0D) to 1D, 2D, and 3D polymeric complexes that depend greatly on the coligands used and show a wide variety of magnetic properties, which have been well reviewed in some reports.[1a,b,c] The second class, which is directly related to this study, however, has limited examples and has not been well developed or explored.[8] The cationic templates could be alkali-metal ions or alkyl ammoniums. The small cations, such as Cs^+ and Me_4N^+, afforded condensed anionic metal–azide frameworks of high dimensionality and connectivity. Examples include $Cs[Mn(N_3)_3]$[8b] and $(Me_4N)[Mn(N_3)_3]$.[8a,c] The former is a NaCl- or perovskite-type framework with EO-azido-bridged Mn_2 dimeric nodes which are further connected by the EE-azido linkages, and the latter compound has octahedral Mn nodes linked by EE-azido bridges. Both compounds have the cations located within the framework cavities and show AF owing to the EE-azido bridges in the structures. $Cs_2[Co_3(N_3)_8]$ possesses anionic Co–azide layers separated by Cs^+ ions. The layer is made of EE-azido-linked chains of alternative apex- and edge-sharing Co_3 triangles with EO-azido edges and $\mu_{1,1,1}$-azido caps.[8e] In $(Me_4N)[Cu(N_3)_3]$,[8a] the Cu–azide chain consists of Cu^{2+} ions bridged by two EE- and one EO-azido anions, and the chains are separated by the cationic columns. This com-

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pound displays ferrimagnetism (FI), probably resulting from the noncompensation between the local magnetic moments of the two non-equivalent Cu^{2+} sites. When large ammonium cations were employed, the generated anionic metal–azide structures were usually low dimensional. The mononuclear paramagnetic complex $(Et_4N)_2[Cu(N_3)_4]$, the dinuclear antiferromagnetic complex $[(nBu)_4N]_2[Cu_2(N_3)_6]$, and the 1D ferromagnetic chains of $[(nPr)_4N]_2[Cu_3(N_3)_8]$[8d] and $(Et_4N)[Mn_2(N_3)_5(H_2O)]$[8b] were synthesized by using large alkyl ammonium cations. It is clear that small cations are favorable for the formation of metal–azide substructures with higher connectivity, while large cations work in the opposite way. It is also of merit to point out that in these compounds, the cationic templates are all monovalent, leaving divalent or polyvalent cationic templates unexplored.

Di- or polyalkylamines, if protonated, could be conveniently used as cationic templates, and they have been widely employed in making metal oxalates, metal phosphates, and oxometalates.[9] Recently, we extended this approach to synthesize magnetic metal formates .[10] On the other hand, the Cu^{2+} ion possesses various coordination geometries to afford complicated Cu–azide compounds in both the structural and magnetic aspects.[4a, 8a, 11] In this study, we have used two protonated diamine cations, N,N'-dimethylethylenediammonium ($dmenH_2^{2+}$) and N,N,N'-trimethylethylenediammonium ($trimenH_2^{2+}$) and successfully synthesized two new Cu–azide compounds, $(dmenH_2)[Cu_6(N_3)_{14}]$ (1) and $(trimenH_2)[Cu_6(N_3)_{14}]$ (2). Both compounds consist of similar condensed Cu–azide layers of *EE*-azido-linked $[Cu_6(N_3)_{14}^{2-}]_n$ anionic chains in which the novel six-membered long-shaped Cu_6 rings are serially connected, and they possess several kinds of Cu–azide–Cu linkages. The cations are located in between the anionic layers. The difference between the two cations is not large, that is, $trimenH_2^{2+}$ has one more methyl group than $dmenH_2^{2+}$. However, tri-

$menH_2^{2+}$ separates the anionic layers better in 2 than $dmenH_2^{2+}$ does in 1, which results in different magnetic properties for the two compounds with respect to the similarity between the two anionic Cu–azide substructures. Long-range antiferromagnetic (AF) ordering and short-range FM are observed in 1, while only short-range FM dominates in 2.

Results and Discussion

Synthesis and IR Spectra

The two compounds possess new condensed Cu–azido layers made of $[Cu_6(N_3)_{14}^{2-}]_n$ anionic chains and separated by the diammonium cations (see below). They were synthesized by employing two slightly different doubly protonated diamines, $dmenH_2^{2+}$ and $trimenH_2^{2+}$, as templates. To the best of our knowledge, these two compounds are the first examples of Cu–azide compounds templated by divalent, protonated diamine cations, though alkyl mono-ammonium cations have been quite widely explored before,[8a,d] and some reports on Cu–azides including diamine as coligands have been found in the literature.[6e, 11a] In our synthesis, the function of using formic acid was twofold: 1) protonating the amine and 2) acting as coligand to form a mixed-ligand system (formate and azide). However, the outcome with only the azido ligand might indicate the better affinity of Cu^{2+} for an azido rather than formato group under our synthetic conditions. Mixed azido/formato systems have been reported by us for other metal ions,[12] and more generally mixed azido/carboxylato compounds are still not popular.[13] The success in synthesizing the two compounds implies that other diamines and polyamines, when protonated, could be used as cationic templates in the construction of new magnetic metal–azide compounds.

The IR spectra of the two compounds (see the Experimental Section and Supporting Information, Figure S1) are quite similar, and display the strong, characteristic bands of the azido bridges and weak bands for the organic cations. For 1, strong bands at about 2080 cm^{-1} are attributed to the $\nu_{as}(N_3)$ absorption and the second strong band at 1279 cm^{-1} to the $\nu_s(N_3)$ absorption.[14] The appearance of these two bands indicate the presence of both *EO*- and *EE*-azido bridges in the structure,[8a] as the structural analysis revealed (see below). Other weak bands could be assigned as follows: 3138 cm^{-1}, C/N−H stretching; 2737 and 2544 cm^{-1}, N−H stretching for -NH_2^+-; 1571 cm^{-1}, N−H bending; 1463 and 1424 cm^{-1}, C−H deformation; 1343 cm^{-1}, -CH_3 symmetric deformation; 1038 cm^{-1}, C−N/C stretching; and 775 cm^{-1}, -CH_2- rocking.[15] All these indicate the existence of the $dmenH_2^{2+}$ cation in 1. The absorption bands for 2 could be easily assigned accordingly.

Structures

Compound 1 crystallizes in the triclinic space group $P\bar{1}$, with one molecule of $(dmenH_2)[Cu_6(N_3)_{14}]$ in the unit cell

Abstract in Chinese：

本工作以质子化二胺阳离子为模板合成了两个铜–叠氮化合物(dmenH₂)[Cu₆(N₃)₁₄] (1) 和(trimenH₂)[Cu₆(N₃)₁₄] (2)，其中，dmenH₂²⁺是双质子化N,N'-二甲基乙二胺，trimenH₂²⁺是双质子化N,N,N'-三甲基乙二胺。这两个化合物具有相同的由不对称的1,3-叠氮桥连[Cu₆(N₃)₁₄²⁻]ₙ阴离子链形成的铜–叠氮阴离子层状结构，而[Cu₆(N₃)₁₄²⁻]ₙ阴离子链的链单元为1,1-叠氮单桥和双桥桥连Cu²⁺离子形成的长形六员环，这些六员环通过1,1-叠氮双桥串联成链，这种铜–叠氮阴离子层状结构鲜有报道。Cu²⁺离子为平面正方形配位，由1,1-叠氮双桥桥连的相邻Cu²⁺离子的基平面基本平行，Cu–N–Cu键角小于103°；由1,1-叠氮单桥桥连的相邻Cu²⁺离子的基平面交角达65–76°，Cu–N–Cu键角大于110°；由不对称的1,3-叠氮桥连的Cu–(1,3-N₃)–Cu扭角为36–71°。这些结构参数导致铜–叠氮层内的铁磁相互作用。结构中铜–叠氮阴离子层之间是质子化二胺阳离子，它们调控了铜–叠氮层间距。2当中层间Cu⋯Cu最短距离9.106 Å，明显比1当中层间Cu⋯Cu最短距离8.016 Å长。层间距的不同造成两种材料不同的磁性行为，1在低温区表现为反铁磁有序，但在高温区主要表现为短程铁磁相互作用；2在2–300 K范围内都表现为短程铁磁相互作用。

(Table 1). The crystal structure consists of layers made of $[Cu_6(N_3)_{14}^{2-}]_n$ anionic chains and dmenH$_2^{2+}$ cations. In the $[Cu_6(N_3)_{14}^{2-}]_n$ anionic chain (Figure 1a), three unique Cu^{2+}

Table 1. Crystallographic data for compounds **1** and **2**.

	1	**2**
Formula	$C_4H_{14}Cu_6N_{44}$	$C_5H_{16}Cu_6N_{44}$
Formula weight	1059.83	1073.86
T [K]	293	293
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	6.9870(2)	11.1127(2)
b [Å]	11.1253(3)	13.3042(3)
c [Å]	11.2423(4)	13.6101(4)
α [°]	76.6913(10)	114.1454(10)
β [°]	87.1756(10)	103.6676(10)
γ [°]	75.053(2)	100.1968(11)
V [Å^3]	821.60(4)	1697.03(7)
Z	1	2
D_c [g cm^{-3}]	2.142	2.102
μ (Mo$_{K\alpha}$) [mm^{-1}]	3.894	3.772
Crystal size [mm^3]	$0.30 \times 0.20 \times 0.15$	$0.64 \times 0.08 \times 0.04$
T_{min} and T_{max}	0.474, 0.566	0.662, 0.865
θ_{min}, θ_{max} [°]	3.45, 27.47	3.42, 27.48
No. of total reflections	15 225	31 711
No. of unique reflections (R_{int})	3735 (0.0594)	7751 (0.0990)
No. of obsd reflections [$I \geq 2\sigma(I)$]	2515	3710
No. of parameters	246	500
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0307, 0.0534	0.0399, 0.0770
$R1$, $wR2$ (all data)	0.0619, 0.0577	0.1185, 0.0914
GOF	0.882	0.850
$\Delta\rho$ [e Å^{-3}][a]	0.399, −0.471	0.554, −0.942
Max. and mean Δ/σ[b]	0.001, 0.000	0.000, 0.000

[a] Max. and min. residual density. [b] Max. and mean shift/sigma.

ions (Cu1, Cu2, and Cu3) are linearly arranged and linked by *EO*-azido ligands, and further linked with the three centrosymmetric equivalent Cu^{2+} ions (at $-x+1$, $-y+1$, $-z+1$) to form an elongated Cu$_6$ ring as the repeat unit of the chain. The two adjacent rings are serially connected at their Cu3 sites by two *EO*-azido bridges along the chain. Within the ring, Cu1 and Cu2 are linked by two *EO*-azido ligands and the other Cu···Cu linkages are single *EO*-azido bridges. The chain or the tape is similar to the tape of our previous reported compound, $[Cu_4(N_3)_8(CH_3CN)_3(bzp)_2]_n$ (bzp = 2-benzoylpyridyl), in which the eight-membered Cu$_8$ rings are linked in serial mode.[4a] All the Cu^{2+} ions are in a square-planar geometry, surrounded by four azido anions, with very small deviations (0.01 to 0.04 Å) out of the basal plane. The basal Cu−N bond lengths are in the range of 1.957–2.022 Å (Supporting Information, Table S1), which is typical for Cu–azide compounds.[6a] The *cis*-N-Cu-N bond angles are in the range 77.6–98.8° and the *trans* angles are between 170.7–174.2°. The Cu-N-Cu bridging angles, the key parameter for Cu···Cu magnetic coupling,[2] are 101.3° and 101.1° for the pair of Cu1-N-Cu2 angles, 111.5° for the single Cu2-N-Cu3 angle, and 116.5° for the single Cu1-N-Cu3 (at $-x+1$, $-y+1$, $-z+1$) angle. Moreover, the two Cu3-N-Cu3 (at $-x+1$, $-y$, $-z+1$) angles between the ring units are equal (102.4°). It is also of merit to point out that the basal planes of Cu1
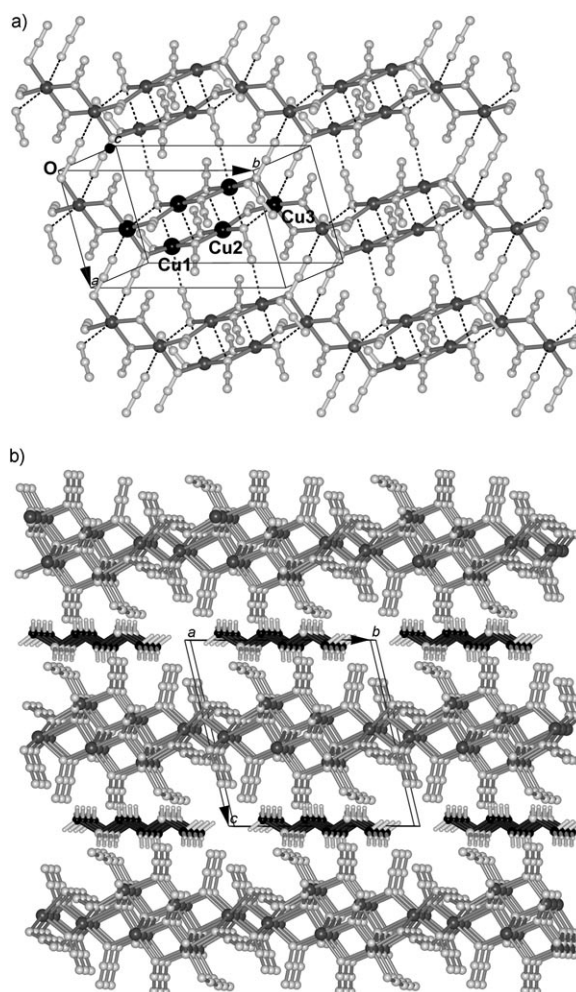

Figure 1. Structure of **1**. a) The anionic Cu–azide layer consisting of $[Cu_6(N_3)_{14}^{2-}]_n$ chains (three in this figure) connected by *EE*-azide linkages (the Cu$_6$ ring is highlighted; Cu medium gray and black; N white). b) Crystal-packing view along the *a* direction. The dmenH$_2^{2+}$ cations are highlighted by dark gray C−C and C−N bonds and black spheres for C atoms.

and Cu2 are nearly coplanar, with a dihedral angle (hereafter denoted δ) of 9.6°. The δ values between the basal planes of Cu2 and Cu3, and Cu1 and Cu3, however, are 74.6° and 65.1°, respectively. These geometric parameters are also related to the magnetism of the compound discussed later. Although all the Cu^{2+} ions are square planar, their axial positions, either one or two, in fact, are occupied by the nitrogen atoms of azido ligands, with the secondary Cu−N bonds of 2.578–2.616 Å (Figure 1a, dashed bonds). If these longer Cu−N bonds are considered, some *EO*-azido anions (four of the seven unique ones) are the $\mu_{1,1,1}$ type, and the chains, which run along the *b* direction, form an anionic layer parallel to the *ab* plane, through $\mu_{1,1,1,3}$ and $\mu_{1,1,3}$ interchain azido anions (Figure 1a). Each Cu$_6$ ring of a chain forms eight of the two kinds of Cu−N$_{azido}$ linkages, with two unique interchain Cu−N separations of 2.585 and 2.616 Å, to the neighboring chains. This condensed Cu–azide layer, to the best of our knowledge, has rarely been found in the

literature.[11c, 16] The asymmetric interchain Cu-N$_3$-Cu linkages through *EE*-azido ligands have torsion angles of Cu-(*EE*-N$_3$)-Cu (hereafter Δ[6]) ranging from 41.0 to 71.1°. The shortest interchain Cu···Cu separation is 5.406 Å within the layer.

The centrosymmetric dmenH$_2^{2+}$ cations are located in between the anionic Cu–azide layers (Figure 1 b). The cation possesses an extended zigzag conformation, and its long axis points in the *b* direction, the same direction in which the [Cu$_6$(N$_3$)$_{14}^{2-}$]$_n$ anionic chain propagates. The cations provide not only the balance in the overall charge of the anionic layers, but also the H bonds, both the N-H···N type (N···N separation 2.82–3.24 Å and N-H···N angle 130–163°) and the C-H···N type (C···N separation 3.25–3.44 Å and C-H···N angle 98–125°), to the azido anions of the layers, and thus connect the anionic and cationic parts of the structure. The good match of the counterparts observed in the structure indicates the template effect of the dmenH$_2^{2+}$ cation in the formation of the structure. The shortest interlayer Cu···Cu separation is 8.016 Å.

Compound **2** also belongs to the triclinic space group $P\bar{1}$, but with a larger unit cell, which is almost double that of **1**, with two molecules of (trimenH$_2$)[Cu$_6$(N$_3$)$_{14}$] per unit cell (Table 1). This is due to the fact that the cation, trimenH$_2^{2+}$, is non-centrosymmetric. The structure is very similar to **1**, possessing an anionic layer made of the [Cu$_6$(N$_3$)$_{14}^{2-}$]$_n$ chains and the trimenH$_2^{2+}$ cations located between the anionic layers (Figure 2). The hexanuclear ring unit now has six unique Cu^{2+} sites, but the molecular geometry of the [Cu$_6$(N$_3$)$_{14}^{2-}$]$_n$ chain around the Cu^{2+} sites (Supporting Information, Table S2) are almost identical to those of **1**, and hence not discussed in detail again. However, the important Cu-N-Cu bridging angles are 99.3–102.6° for the Cu···Cu linkages with double *EO*-azido bridges, and 110.2–114.5° for those with a single *EO*-azido bridge. Again, the two Cu^{2+} ions in each linear trinuclear moiety within the Cu$_6$ ring, that is, Cu2 and Cu3, and Cu5 and Cu6, have their basal planes nearly coplanar ($\delta = 10.6$ and 8.7°), while they are twisted relative to the basal planes of Cu1 and Cu4, which are the connections of the hexanuclear ring units along the chain ($\delta = 66.0$–76.1°).

Although the anionic Cu–azide chain and the layer of **2** are very similar to that of **1**, the non-centrosymmetric trimenH$_2^{2+}$ cation, with one more methyl group, seems to separate the chains to a small extent but separates the layers to a more significant extent. In the layer of **2** (Figure 2 a), each Cu$_6$ ring unit of one chain also has long interchain Cu-N$_{azido}$ linkages through the $\mu_{1,1,1,3}$ and $\mu_{1,1,3}$ interchain azido anions to the neighboring chains, but the interchain Cu-N separations are 2.545 and 2.626 Å on one side of the chain, and 2.626 and 2.738 Å on the other side, and the torsion angles Δ are between 36.0 and 68.3°. Notably, the interchain separation is not uniform in the layer (Figure 2 a), unlike the uniform separation (Figure 1 a) observed in the layer of **1**. The trimenH$_2^{2+}$ cations are in centrosymmetric pairs, and the main chain of the cation is in an extended conformation, and runs parallel to the [Cu$_6$(N$_3$)$_{14}^{2-}$]$_n$ chain that propagates along the *a* direction. The pairing of cations would result in
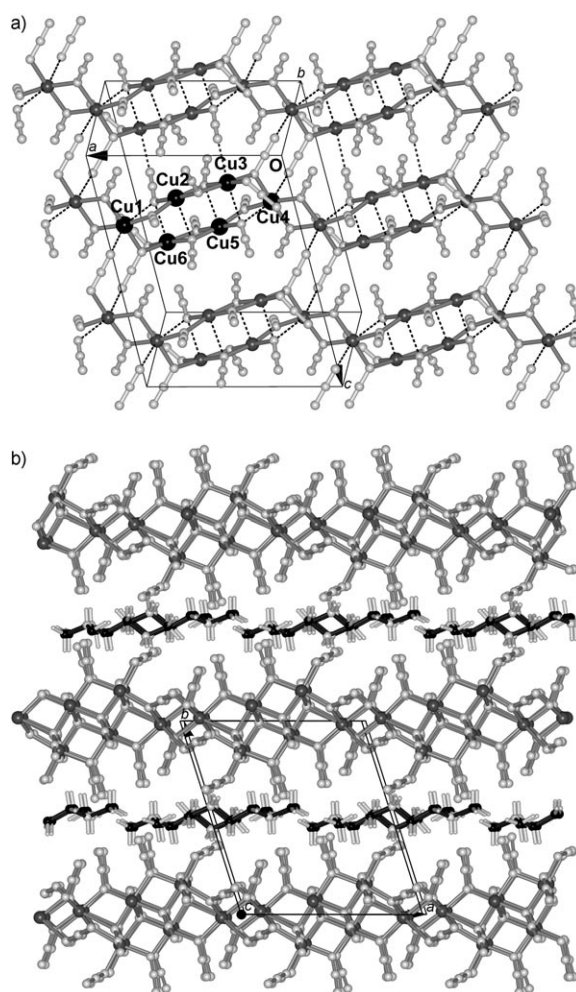

Figure 2. Structure of **2** in the same style used in Figure 1. a) The anionic Cu–azide layer. b) Crystal-packing view along the *c* direction.

the nonuniform interchain separation within the anionic Cu–azide layer. The cations bring the anionic layers together to form a 3D architecture through the C/N-H···N$_{azido}$ H bonds (N···N separation 2.79–3.06 Å and N-H···N angle 125–176°, and C···N separation 3.17–3.47 Å and C-H···N angle 100–171°). The shortest interlayer Cu···Cu separation is significantly longer in **2** (9.106 Å) than in **1** (8.016 Å).

Magnetic Properties

In spite of the similarity in the anionic Cu–azide substructures in **1** and **2**, the two compounds show different magnetic behaviors. Compound **1** displays a global long-range AF ordering in the low-temperature region but short-range FM in the high-temperature region (Figure 3). Under an applied field of 1 kOe, the χT value of 2.78 cm^3 K mol^{-1} (per Cu$_6$) at 300 K is expected for six uncoupled Cu^{2+} ions with $S = 1/2$.[17] The χT value gradually increased to a broad maximum of 2.92 cm^3 K mol^{-1} around 100 K, then decreased quickly as the temperature was further lowered and finally
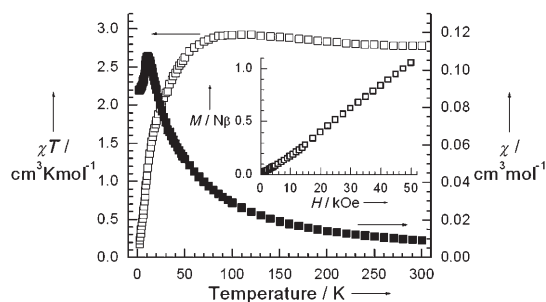
Figure 3. Plots of χ and χT versus T for **1** under 1 kOe field. Inset: Isothermal magnetization at 2 K.

reached a value of 0.18 cm³ K mol⁻¹ at 2 K. This behavior of **1** indicates predominant ferromagnetic (FM) interaction within the material at high temperatures, FM–AF magnetic competition around 100 K, and finally global AF in the low-temperature region. The magnetic susceptibility data above 120 K were fitted by the Curie–Weiss law (Supporting Information, Figure S2), which gave a Curie constant of 2.67 cm³ K mol⁻¹ and a Weiss temperature of +11.5 K. The positive Weiss temperature confirms the dominant FM interactions in the high-temperature region. Moreover, a maximum of χ is observed at 11.0 K, suggesting long-range AF ordering. The Néel temperature, T_N, determined by the peak position of d(χT)/dT, was 8.5 K. At 2 K, the isothermal magnetization increased slowly and linearly with the applied magnetic field and reached a value of 1.05 Nβ at 50 kOe (Figure 3, inset), far below the expected saturation value (6.0 Nβ for 6 Cu²⁺ assuming $g = 2.00$), which confirms the AF ground state at low temperature.

The magneto–structural correlation for Cu–azide has been studied in detail both experimentally and theoretically.[2, 4, 6] For two Cu²⁺ ions bridged by a *EO*-azido linkage, it is well established that the magnetic coupling between the two Cu²⁺ ions could be either FM or AF, which depends on the Cu-N-Cu bridging angle, provided the two basal planes of Cu²⁺ ions are coplanar. The critical angle for the transition from FM (for smaller Cu-N-Cu angles) to AF (for larger Cu-N-Cu angles) obtained from theoretical calculations is 104° and 108° from experiment data.[2] On the basis of the structure of **1** and the molecular geometries discussed above, it is safe to say that the magnetic exchange is FM between Cu1 and Cu2, Cu3 and Cu3 (at $-x+1$, $-y$, $-z+1$) with double *EO*-azido bridges, as the Cu-N-Cu angles are smaller than 104° and the Cu basal planes are nearly coplanar. For the two single *EO*-azido-bridged Cu pairs, Cu1 and Cu3 (at $-x+1$, $-y+1$, $-z+1$), and Cu2 and Cu3, the Cu-N-Cu angles (111.5° and 116.5°) are larger than the critical angle, but the two Cu basal planes are twisted relative to each other in each pair, with the dihedral angles δ being 65.1° and 74.6°. In this case, the magnetic exchange in the two pairs could be FM but not AF because the large δ leads to a small overlap integral between the local magnetic orbitals, as revealed by our study of the compound $[Cu_4(N_3)_8$ $(CH_3CN)_3(bzp)_2]_n$,[4a] in which similar *EO*-azido-bridged Cu₂

pairs with Cu-N-Cu angles of 116.4–116.8° and δ angles of 68.9–72.8°, in fact, transmit FM interaction, based on DFT-BS calculations and experimental data, with a coupling of +29 cm⁻¹. According to these analyses, the magnetic interactions between the Cu²⁺ sites within the $[Cu_6(N_3)_{14}{}^{2-}]_n$ chain are all FM and thus the chain is ferromagnetic. The chains are connected to the layers through the asymmetric interchain Cu-(*EE*-N₃)-Cu linkages with the torsion angles, Δ, between 41.0 and 71.1°. These linkages, according to the previous work by Robert et al.,[6] should transmit FM exchanges in between the chains within the layer. Therefore, the anionic Cu–azide layer is FM in **1**, and this explains the fact that the compound displays predominant FM in the high-temperature region. The global AF state in the low-temperature region may result from the AF interaction between the FM layers separated with the shortest interlayer Cu···Cu separation of 8.016 Å. Over such a short distance, dipole–dipole as well as exchange effects through H bonds might be possible, and the interlayer magnetic interactions may be mediated by interlayer H bonds. Although some results[18] have been reported, the role of H bonds in mediating magnetism is still not clear.

Only dominant FM interaction was observed for **2** in the whole temperature range of 2–300 K (Figure 4). At 300 K, the χT value of 3.01 cm³ K mol⁻¹ per Cu₆ unit was significantly larger than the value expected for six uncoupled Cu²⁺ ions. Upon lowering the temperature, the χT value increased continuously and quickly and finally reached a value of 11.14 cm³ K mol⁻¹ at 2 K. The magnetic susceptibility data above 120 K fit the Curie–Weiss law well (Supporting Information, Figure S2), and gave a Curie constant of 2.71 cm³ K mol⁻¹ and a Weiss temperature of +30.3 K. The large positive Weiss temperature confirms the strong, dominant FM within the material. Moreover, at 2 K, the field-dependent magnetization initially increased quickly to 3.8 Nβ in the low-field region, and above 10 kOe, it increased slowly and linearly with the applied field and reached 5.0 Nβ at 50 kOe (Figure 4, inset), which was a little below the expected saturation value (6.0 Nβ for Cu²⁺ assuming $g = 2.00$). This confirmed the FM characteristics of **2**, though the magnetization does not saturate even at the highest applied field of 50 kOe.
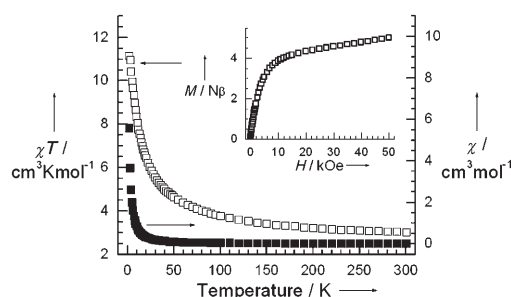

Figure 4. Plots of χ and χT versus T for **2** under 1 kOe field. Inset: Isothermal magnetization at 2 K.

Compound **2** possesses a very similar anionic Cu–azide layer structure to that of **1**, and thus the exchange interaction within the layer is FM. The significant difference lies in the fact that the anionic magnetic layers are separated better by the larger cations (trimenH$_2^{2+}$) in **2** than by the smaller cations (dmenH$_2^{2+}$) in **1**, with the shortest interlayer Cu···Cu separation being 9.106 Å in **2** versus 8.016 Å in **1**. In the case of **2**, the longer separation between the FM layers might contribute to the dipole–dipole FM interaction without long-range ordering.[19] Therefore, **1** and **2** show cation-tuned magnetism based on the similar magnetic Cu–azide substructures. The crossover from the interlayer AF interaction in **1** to the interlayer FM interaction in **2** might result from the competition between exchange (or orbital) effects favoring AF interaction when the layers are close to each other and dipolar effects favoring FM interaction when the layers are farther apart. Such behavior was also observed in a series of 2D A$_2$Mn$_2$[Cu(opba)]$_3$·$n$solv (A = alkali-metal cation, radical cation, or tetraalkylammonium, opba = orthophenylenebis(oxamato), solv = solvent),[20a] where small cations favor metamagnetic behavior with long-range antiferromagnetic ordering, while large cations favor long-range ferromagnetic ordering. The modulation of magnetism by the separation between the magnetic layers has been reported for some pillared layer compounds,[16,20] and, in particular, cation-modulated magnetism for the compounds with the same or similar magnetic substructures has been observed in only a few other systems such as the series of 2D oxalato-bridged complexes, MPS$_3$ (layered transition-metal hexathio-hypodiphosphate) ion-intercalation compounds,[20b] and the systems of 3D frameworks of (amineH$^+$)[Mn(HCOO)$_3$] (amineH$^+$ = protonated alkyl monoamine cations).[21]

Conclusions

In summary, using two different protonated diamine cations, dmenH$_2^{2+}$ and trimenH$_2^{2+}$, as cationic templates, two new Cu–azide compounds, (dmenH$_2$)[Cu$_6$(N$_3$)$_{14}$] and (trimenH$_2$)[Cu$_6$(N$_3$)$_{14}$], were successfully obtained. The two compounds possess similar condensed Cu–azide layers consisting of [Cu$_6$(N$_3$)$_{14}^{2-}$]$_n$ anionic chains linked by asymmetric *EE*-azido bridges, where the chain is a new type with serially linked elongated Cu$_6$ rings with double and single *EO*-azido linkages between the Cu^{2+} sites within the ring and double *EO*-azido bridges serially connecting the rings. The cations are located in between the anionic Cu–azide layers and also separate them. The magneto–structural relation revealed that the magnetic interaction within the layers in both the compounds is ferromagnetic. However, owing to the different interlayer separations, **1** displayed long-range antiferromagnetic ordering in the low-temperature region and short-range ferromagnetism at high temperatures, while only short-range ferromagnetism was observed in **2**. These two examples demonstrate that new magnetic metal–azide compounds could be synthesized by the use of other protonated diamines and polyamines as cationic templates, and cation-

tuned magnetism could be obtained from similar magnetic substructures.

Experimental Section

Synthesis

All reagents were commercially available and were used as received. All reactions were carried out under aerobic conditions.

CAUTION! Although not encountered in our experiments, azide and perchlorate compounds are potentially explosive. Only a small amount of the materials should be prepared, and they should be handled with care.

(dmenH2)[Cu$_6$(N$_3$)$_{14}$] (**1**): An aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (94 mg in 3.0 mL) was placed at the bottom of a glass tube. On top of it, water (3.0 mL) was carefully layered, followed by careful layering of an aqueous solution (10 mL) of HCOOH (50 mg), NaN$_3$ (65 mg), and *N,N'*-dimethylethylenediamine (dmen, 24 mg). The tube was then sealed and kept undisturbed. Half a day later tiny blocklike crystals appeared on the interface. Crystallization took one week and gave crystals of **1** (43% yield based on Cu(ClO$_4$)$_2$·6H$_2$O). The product was washed with methanol and dried in air. IR data: $\tilde{\nu}$ = 3597 (br, w), 3311 (w), 3138 (b), 2737 (br, w), 2544 (br, w), 2087 (vs), 2075 (vs), 1571 (w), 1463 (w), 1424 (w), 1343 (w), 1279 (m), 1038 (w), 868 (w), 775 (w), 685 cm^{-1} (w); elemental analysis: calcd (%) for C$_4$H$_{14}$N$_{44}$Cu$_6$: C 4.53, H 1.33, N 58.16; found: C 4.82, H 1.80, N 57.63.

(trimenH$_2$)[Cu$_6$(N$_3$)$_{14}$] (**2**): An aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (94 mg in 6.0 mL) was placed on one side of an H-shaped tube, while an aqueous solution (6.0 mL) of HCOOH (45 mg), NaN$_3$ (65 mg), and *N,N,N'*-trimethylethylenediamine (trimen, 26 mg) was placed on the other side. Water (6.0 mL) was layered on the solutions on both sides to provide a diffusion pathway. Crystallization took one week and gave crystals of **2** (30% yield based on Cu(ClO$_4$)$_2$·6H$_2$O). IR data: $\tilde{\nu}$ = 3611 (br, w), 3338 (w), 3158 (w), 2786 (br, vw), 2540 (br, vw), 2102 (vs), 1579 (w), 1464 (w), 1345 (w), 1283 (m), 1000 (w), 778 (w), 688 cm^{-1} (w); elemental analysis: calcd (%) for C$_5$H$_{16}$N$_{44}$Cu$_6$: C 5.59, H 1.50, N 57.40; found: C 6.03, H 1.77, N 56.59.

X-ray Crystallography and Physical Measurements

Crystallographic data for **1** and **2** were collected at 293 K on a Nonius KappaCCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å.).[22] Empirical absorption corrections were applied using the Sortav program.[23] The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELX[24] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were added geometrically and refined using the riding model. Crystallographic data and structure refinement results are summarized in Table 1. Selected molecular geometries are listed in the Supporting Information, Tables S1 and S2. CCDC-673132 (**1**) and 673133 (**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.

Element analysis was performed on an Elementar Vario El analyzer. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan microscope for pure samples. Magnetic measurements were performed on a Quantum Design MPMS XL5 SQUID system for polycrystalline samples, which were tightly packed and sealed in a capsule. Diamagnetic corrections were estimated using Pascal parameters[25] and background correction by experimental measurement on the sample holder.

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