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Unprecedented Self-Catenated Eight-Connected Network Based on Novel Azide-Bridged Tetramanganese(II) Clusters

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The combination of the azide bridge and a neutral inner-salt-type dicarboxylate ligand leads to a three-dimensional coordination framework that contains unprecedented azide-bridged tetramanganese(II) clusters and defines a novel self-catenated, eight-connected net of $4^{16} \cdot 6^{12}$ topology.

Polymeric coordination networks are currently of great interest for their intriguing and diverse architectures and for their potential applications as functional materials.[1,2] Some recent attention has been paid to the construction of highly connected, three-dimensional (3D) networks (connectivity >6).[3−5] This is a challenging task because of the limited coordination sites around metal centers and the steric hindrance between ligands. Schröder and others have obtained a few seven- and eight-connected networks, making use of the high coordination numbers of lanthanides and the small steric hindrance of bis(pyridine-*N*-oxide)-type linkers.[3] A different approach is to use polynuclear clusters as decorated nodes, which can have a higher number of outward-connecting sites and a larger surface that can accommodate more ligands.[4] Recently, a few eight-connected nets based on metal carboxylate clusters have been reported.[5,6a,b] Another theme of interest to network construction is supramolecular entanglement, which contributes much to the structural diversity of coordination networks.[2a,7] Self-penetration (or self-catenation) is a peculiar type of entanglement in which the smallest topological circuits from the same network are catenated with each other. This phenomenon has evoked increasing interest recently,[6,7b] but its occurrence is still rare and the design is still a formidable challenge to chemists.

We have been interested in the design of molecular magnetic materials using azide and appropriate coligands.[8a,b] Azide can adopt various bridging modes (μ_2-1,1, μ_2-1,3, μ_3-1,1,1, etc.) and has led to various networks with interesting magnetic properties.[8] Recently, many metal azide clusters (usually with cobridges), including a few single-molecule magnets, have been reported.[9] However, no 3D networks based on metal azide clusters with three or more metal ions have been described. Here we report the synthesis, structure, and magnetic properties of a novel coordination polymer of formula $[Mn_4(L)_2(N_3)_8]_n$ (**1**), where L is a neutral inner-salt-type dicarboxylate ligand, 1,3-bis(4-carboxylatopyridinium)propane (Figure 1a). The compound is unique in two

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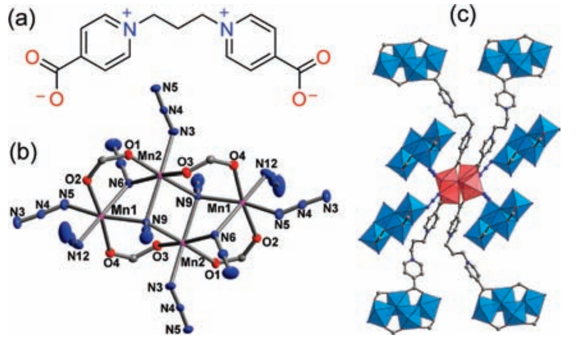

Figure 1. Views showing (a) the ligand, (b) the tetranuclear cluster (thermal ellipsoids are drawn at 30% probability), and (c) the connection of a cluster with eight neighbors in **1**.

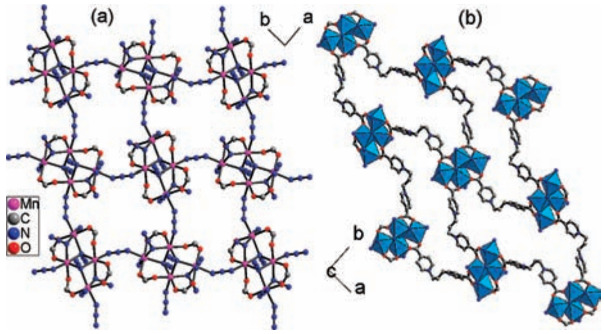

Figure 2. Views showing the different (4,4) networks formed by connecting the clusters with azide (a) and L (b) linkers, respectively.

aspects: (i) It contains an unprecedented [$Mn_4(\mu_3\text{-}1,1,1\text{-}N_3)_2(\mu_2\text{-}1,1\text{-}N_3)_2(\mu_2\text{-}COO)_4$] cluster. (ii) The clusters are cross-linked by μ_2-1,3-N_3 and bis(pyridinium)propane to give a 3D network, which defines an unprecedented eight-connected, self-catenated topology.

Compound **1** was prepared by slow evaporation.[10] X-ray analysis[11] revealed a 3D structure based on tetranuclear clusters. The cluster contains a centrosymmetric $[Mn_4(N_3)_2]^{6+}$ core, in which four Mn^{II} atoms are linked by two equivalent azide bridges in the μ_3-1,1,1 mode to form a planar rhombus. The geometry can also be described as two coplanar Mn3 triangles sharing an edge, which is defined by two Mn2 atoms doubly bridged by μ_3-N_3, with Mn···Mn = 3.305 Å and Mn−N−Mn = 92.80(7)°. The μ_3-N atoms (N9) are displaced above and below the Mn_4 plane by 1.03 Å, and the sum (301.6°) of the three M−N−M angles around each μ_3-N deviates much from 360°, defining a flat pyramidal shape for the Mn_3N moiety. There are two different bridging motifs between Mn1 and Mn2 atoms. One is a triple-bridging motif consisting of a μ_3-azide [Mn2−N9−Mn1 = 92.27(7)°], a μ_2-1,1-azide [Mn1−N6−Mn2 = 97.30(8)°], and a μ_2-carboxylate (O1−C−O2, in the syn,syn mode), with Mn···Mn = 3.333 Å, while the other is a double-bridging motif with a μ_3-azide [Mn1−N9−Mn2 = 116.48(8)°] and a μ_2-carboxylate (O3−C−O4, also in the syn,syn mode), with a significantly longer Mn···Mn distance (3.935 Å). Both Mn1 and Mn2 adopt the pseudooctahedral [MN_4O_2] geometry, completed by the above-mentioned μ_3-azide, μ_2-1,1-azide, and μ_2-carboxylate and additional azides in different coordination modes (N12−N13−N14, terminal; N3−N4−N5, μ_2-1,3), with Mn−N/O ranging from 2.12 to 2.34 Å. The two carboxylate O atoms (O2 and O4) for Mn1 are in trans positions, while those (O1 and O3) for Mn2 in are in cis positions. Such a cluster is reminiscent of the well-known clusters $[M_4(\mu_3\text{-}O)_2(\mu_2\text{-}COO)_6]^{n+}$ ($n = 0-2$; M = Mn, Fe, Cr), which have been extensively studied for decades because of their great relevance to biological systems and magnetic materials.[12] A major difference is that the previous clusters contain high-valence metals (mixed-valent $M^{II}M^{III}$ or homovalent M^{III}). When this difference is neglected, the present manganese(II) cluster can be generated by replacing the μ_3-O^{2-} bridges and two of the μ_2-COO bridges in the previous clusters with μ_3- and μ_2-1,1-azide bridges, respectively. Such a Mn^{II}_4 cluster is unprecedented, although some clusters with mixed carboxylate and azide bridges have been reported.[9]

The cluster possesses eight bridging ligands (four μ_2-1,3-azides and four L ligands) sticking out for intercluster connection and, hence, acts as an eight-connecting node (Figure 1c). The connection of clusters through the μ_2-1,3-azides, which separate Mn1 and Mn2 from different clusters by 5.915 Å, leads to a two-dimensional (2D) (4,4) square grid layer along the (001) plane (Figure 2a). It is noted that the clusters in the layer are alternately arranged in two different orientations. To form the 3D framework, the L ligand serves as a bis(μ_2-COO) bridge to link two clusters from neighboring azide-bridged layers. In fact, each cluster is linked to four clusters by four L ligands, generating L-bridged 2D rhombic (4,4) networks (Figure 2b), with the center-to-center distance (18.70 Å) between the nodes being much longer than that (10.42 Å) in the azide-bridged network. To adapt to the two different orientations of the clusters, there are two equivalent L-bridged networks along different planes, (102) and (−102). As simplified in Figure 3a, the azide-bridged (4,4) net (green) shares nodes (Mn_4 clusters) with two sets of L-bridged (4,4) nets of different orientations (red and blue), defining a novel self-catenated, eight-connected uninodal 3D net of $4^{16}\cdot 6^{12}$ topology.[13a]

It is desirable to analyze how the structure of **1** is different from the well-known body-centered-cubic lattice (bcu or CsCl net, $4^{24}\cdot 6^{4}$) and previously known self-catenated, eight-connected structures. So far, only three self-catenated, eight-connected coordination nets have been reported very recently: $4^{24}\cdot 5\cdot 6^{3}$ based on $[Zn_5(\mu_3\text{-}OH)_2(COO)_8]$,[6a] $4^{20}\cdot 6^{8}$ based on [$Cd_3(COO)_6$(N-donor)$_2$],[6b] and $4^{24}\cdot 6^{4}$ based on [$Cu_4V_4O_{12}$(N-donor)$_8$].[6c] All of these are based on neutral cluster nodes and the usual dicarboxylate and/or bis(N-donor) linkers. The

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(10) Synthesis: A mixture solution of $Mn(OAc)_2\cdot 4H_2O$ (0.049 g, 0.2 mmol), L·2HBr (0.0448 g, 0.1 mmol), and NaN_3 (0.065 g, 1.0 mmol) in water (2 mL) and ethanol (4 mL) was allowed to stand at room temperature, and red crystals of **1** were obtained in 1 week. Yield: 27.5% based on L. Anal. Calcd for $C_{30}H_{28}Mn_4N_{28}O_8$: C, 31.9; H, 2.5; N, 34.7. Found: C, 31.9; H, 2.9; N, 34.5. IR (cm^{-1}, KBr): 2076s, 2038s, 1619s, 1563m, 1449m, 1396s, 778m. The phase purity of the bulk sample was confirmed by powder X-ray diffraction.

(11) Crystal data for **1**: $C_{30}H_{28}Mn_4N_{28}O_8$, M_r = 1128.56, orthorhombic, *Pbca*, a = 13.7371(5) Å, b = 15.6580(5) Å, c = 19.9617(7) Å, V = 4293.7(3) Å^3, Z = 4, μ(Mo Kα) = 1.234 mm^{-1}, ρ_{calcd} = 1.746 g cm^{-3}, S = 1.014, R1 = 0.0562 and wR2 = 0.0874, for 4970 unique reflections (R_{int} = 0.0500), T = 296(2) K.

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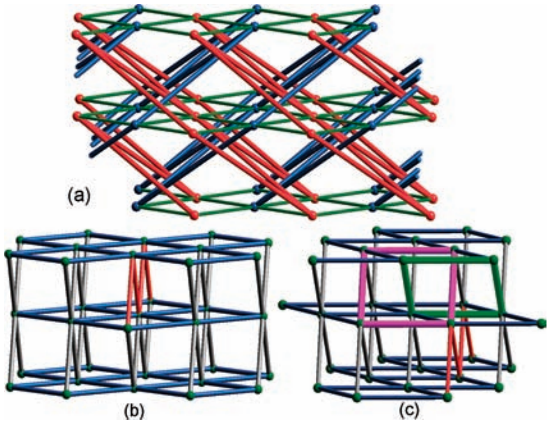

Figure 3. Views showing (a) the self-catenated net of **1**, (b) the bcu net (an interlayer zigzag chain is highlighted by red lines), and (c) the self-catenated $4^{24}\cdot5\cdot6^3$ net (the catenation is exemplified by purple and green rings, and an interlayer zigzag chain is highlighted by red lines).

net of **1** is unique in that it is based on azide-bridged anionic clusters $[Mn_4(N_3)_8(COO)_4]^{4-}$ and cationic pyridinium linkers.

All of the above nets can be described as parallel (4,4) layers being cross-linked by zigzag chains,[3a,6] but the connection modes are different. In bcu and the previous self-catenated nets, the zigzag chains between two adjacent layers are all parallel. In bcu (Figure 3b), the zigzag chain bridges across the diagonal of a single [2 × 2] window of the (4,4) layer, and no self-catenation occurs. In the three previous self-catenated nets, self-catenation results from the unusual connection modes that the zigzag chain bridges across the diagonal of two, six, or eight [2 × 2] windows (the windows define a [2 × 3], [3 × 4], or [3 × 5] grid, respectively. The numbers in square brackets refer to the numbers of nodes in the grid along two different directions). This is exemplified by the $4^{24}\cdot5\cdot6^3$ net (the three-letter code is ilc[13b]) in Figure 3c. The self-catenation in **1** is completely different. As observed in bcu, the zigzag chain bridges across the diagonal of a single window of the (4,4) layer (green in Figure 3a), but there are two sets of interlayer zigzag chains that are inclined with respect to each other and alternately link the nodes in the (4,4) layer. Such an unusual connection inevitably causes self-catenation. A better insight into the catenation in **1** can be achieved by considering the net as follows. The long L ligands interlink the clusters into two equivalent but nonparallel sets of (4,4) layers (red and blue in Figure 3a), and this inevitably leads to inclined interpenetration:[2b,7a,b] each rhombic ring of one layer set is catenated by four identical rings from two layers belonging to the other set. The 3D net of **1** can be obtained by cross-linking the two layer sets with short μ-1,3-azide bridges, which connect each node of one layer set to four neighboring nodes belonging to the other set.

The observation of the peculiar self-catenation in **1** benefits from the following important factors, among others. The first is the capability of azide and carboxylate to form clusters, although the rational design of clusters is impossible at the current stage. The second is the use of the neutral inner-salt dicarboxylate ligand. The positively charged pyridinium groups serve to compensate for the anionic $[Mn_4(N_3)_8(COO)_4]^{4-}$ cluster (a negative dicarboxylate ligand would require extra space-filling cations that are unfavorable to catenation), and the flexible $(CH_2)_3$ spacer affords enough structural adaptability. Third, the unique combination of the short (azide) and long (L) linkers seems to be critical. Finally, we want to emphasize the importance of the μ-1,3-azide bridge. This bridge is usually asymmetric and tends to relatively incline the coordination spheres that it links. The significance of this feature has been noted in the design of magnetic materials.[8b,d] In **1**, the asymmetric bridge makes the neighboring clusters relatively inclined, which results in nonparallel interlayer zigzag connections and hence the self-catenation.

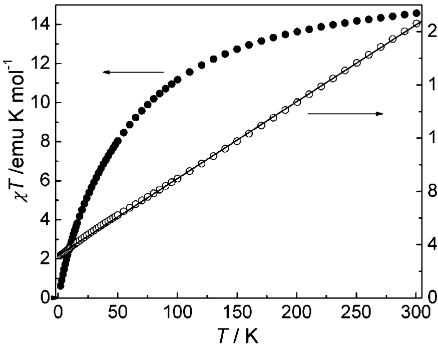

Figure 4. χT and χ^{-1} vs T plots for **1**. The line represents the fit to the Curie−Weiss law.

Magnetic measurements were performed on **1** (Figure 4). The χT value (χ = molar susceptibility) per formula at 300 K is 14.58 emu mol^{-1} K, significantly lower than the spin-only value (17.5 emu mol^{-1} K) for four isolated Mn^{II} ions. Upon cooling, χ and χT exhibit monotonic increase and decrease, respectively. The data above 15 K follow the Curie−Weiss law, with $\theta = -57.8$ K and $C = 17.48$ emu mol^{-1} K. The C value is in good agreement with the spin-only χT value, and the negative θ value suggests an overall antiferromagnetic behavior. This is confirmed by the isothermal magnetization measurement at 2 K (see the Supporting Information). Because of the lack of an appropriate model for such a complex system, we cannot quantitatively evaluate the interactions through the different bridges.

In summary, we have characterized a novel self-catenated, 3D network with unprecedented azide-bridged tetramanganese(II) clusters as eight-connecting nodes. The formation of the net benefits from the unique combination of azide bridges and zwitterionic dicarboxylate ligands. The discovery of this new net enriches our knowledge of structural topologies and may suggest the great potential of constructing new highly connected and/or self-catenated networks from metal azide clusters.

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

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