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Supramolecular Engineering of a 2D Kagomé Lattice: Synthesis, Structures, and Magnetic Properties

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Two 2D Mn^{II} complexes, $[Mn_3(TzDC)_2(phen)_3]\cdot 2H_2O$ (**1**; H_3TzDC = 1,2,3-triazole-4,5-dicarboxylic acid, phen = 1,10-phenanthroline) and $[Mn_3(TzDC)_2(bipy)_3]\cdot 4H_2O$ (**2**; bipy = 2,2′-bipyridine), were synthesized by hydrothermal reactions and characterized magnetically, and complex **1** was the first example of the chiral complex with a Kagomé lattice connectivity obtained through spontaneous resolution.

Geometrically frustrated magnetic lattices where frustration arises from incompatibility of the local antiferromagnetic (AF) interactions with the global symmetry imposed by the crystal lattice have been a subject of recent experimental and theoretical studies.[1] The two-dimensional (2D) Kagomé lattices consist of corner-sharing triangles of spins with AF coupling between nearest neighbors, with the adjacent triangles sharing only one lattice point in common.[2,3] Up to now, however, the magnetic properties of Kagomé lattices remain poorly characterized partly because it is difficult to prepare such complexes with Kagomé lattices.[4] Most of the Kagomé complexes investigated belong to the family of iron jarosites and their analogues, which exhibit a geometric magnetic frustration, and some show long-range AF ordering and even ferromagnetic features.[5] For the metal−organic Kagomé lattices, two synthetic approaches are usually applied: (I) One route is to use the bridging ligand to connect metal centers into linear secondary building units (SBUs).[6] Recently, a Mn^{II} complex with a Kagomé lattice with pseudohalide ligands (azides) was reported to show long-range ordering and a spin-glasslike behavior. The Kagomé lattice with the paramagnetic dicopper(II) tetracarboxylate spin pairs (metal dimers) positioned at the vertices was also constructed by linking carboxylate bridges.[2c,7] (II) The other interesting synthetic route for structural optimization is to introduce paramagnetic triangular SBUs, in which a three-connected ligand bridges three metal ions in a triangular arrangement similar to the $Fe^{III}_3(\mu\text{-}OH)_3$ triangles in jarosites (Scheme 1). Then the triangular trinuclear building units can be employed as a module in the construction of Kagomé layers by sharing the corners.[8] For example, tricyanomethanide $[C(CN)_3]^-$, which can bind to three metal sites, leads to the formation of geometrical spin-frustration coordination complexes.[9] Other organic ligands such as 1,2,3-triazole-4,5-dicarboxylic acid (H_3TzDC) are also good candidates for Kagomé layers because of the triangular arrangement for the three-connected rigid-jointed planar

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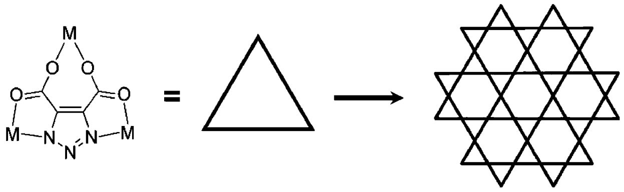
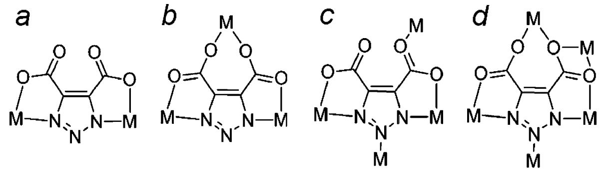
Scheme 1. Illustration of Triangular SBUs That Can Be Linked Together To Form a 2D Kagomé Lattice



Scheme 2. Most Frequently Occurring Coordination Modes of $TzDC^{3-}$



$[M_3L]$ SBUs (Scheme 2b).[8,10] Herein we report the synthesis, crystal structures, and magnetic properties of two polymeric networks: $[Mn_3(TzDC)_2(phen)_3]\cdot 2H_2O$ (**1**; phen = 1,10-phenanthroline) and $[Mn_3(TzDC)_2(bipy)_3]\cdot 4H_2O$ (**2**; bipy = 2,2′-bipyridine). Complex **1** is the first example of the chiral complex with a Kagomé lattice obtained through spontaneous resolution.

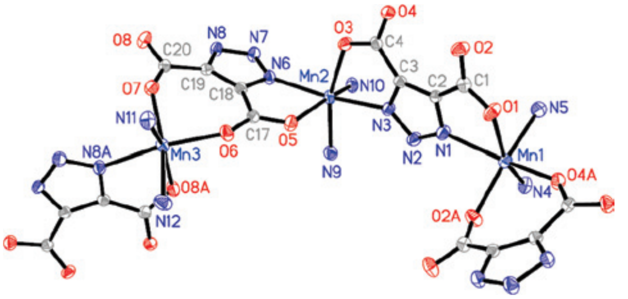


Figure 1. View of the coordination sphere in complex **1** (the C atoms of phen are omitted for clarity). Selected bond distances (Å) and angles (deg): Mn1−O1 2.185(2), Mn1−N1 2.269(2), Mn2−O3 2.179(2), Mn2−N3 2.213(2), Mn3−N8B 2.292(2), Mn3−N11 2.264(3); O2A−Mn1−O1 115.1(1), N4−Mn1−N1 101.2(1), O5−Mn2−N10 158.8(1), O5−Mn2−N3 98.2(1), N7−N8−Mn3C 139.9(2), N11−Mn3−N12 72.0(1), C4−O4−Mn1D 142.2(2). Symmetry codes: A, $x - {}^1/_2$, $-y + {}^1/_2$, $-z + 1$; B, $-x - {}^1/_2$, $-y + {}^1/_2$, $-z + 2$; C, $x + {}^1/_2$, $-y + {}^1/_2$, $-z + {}^1/_2$; D, $x + {}^1/_2$, $-y + {}^1/_2$, $-z + 1$.

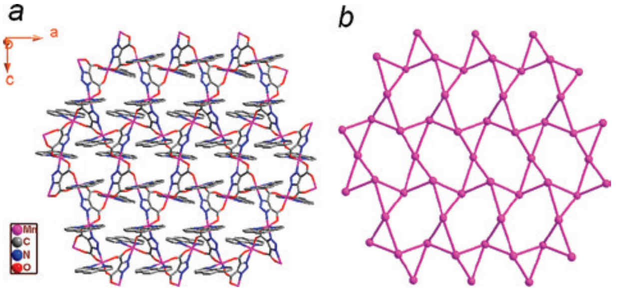


Figure 2. (a) 2D sheet along the *ac* plane in **1**. (b) Kagomé lattice (each Mn atom as a node) in complex **1**.

The light-yellow crystals of **1** were obtained through the hydrothermal reaction of $MnCl_2\cdot 4H_2O$, phen, and H_3TzDC prepared from oxidation of benzotriazole. Single-crystal X-ray diffraction analysis of **1** reveals an infinite 2D coordination network with a Kagomé lattice that crystallizes in the chiral space group $P2_12_12_1$. [Crystal data **1**: $C_{44}H_{28}N_{12}Mn_3O_{10}$, $M_r = 1049.60$, orthorhombic, space group $P2_12_12_1$, $a = 9.8878(2)$ Å, $b = 20.1939(3)$ Å, $c = 21.1225(4)$ Å, $V = 4217.60(13)$ Å^3, $T = 293$ K, $Z = 4$, μ(Mo Kα) = 0.962 mm^{-1}, 56 610 reflections measured, 9681 unique ($R_{int} = 0.0625$), R1 = 0.0391, wR2 = 0.0923 (all data), Flack value = 0.159(12). CCDC 676344 for **1**. The powder X-ray diffraction pattern for **1** is shown in Figure S1 in the Supporting Information.] The asymmetric unit contains three Mn^{II} ions, and all of the Mn centers in **1** are chiral with three chelating ligands. The chiral metal centers are related by three 2-fold screw axes along three directions; the whole structure is thus chiral. Although crystallographically independent, Mn1 and Mn3 are essentially identical in other aspects. Mn1 and Mn3 are coordinated with two carboxylate O atoms from two different carboxylates of the same $TzDC^{3-}$ ligand, two N atoms from a phen ligand, one carboxylate O atom, and one triazole N atom, generating a slightly distorted octahedral geometry. Mn2 is coordinated with two N atoms from a phen ligand and two bidentate fragments including a carboxylate O atom and a triazole N atom from two different $TzDC^{3-}$ ligands, producing a slightly distorted octahedral geometry (Figure 1). $TzDC^{3-}$ ligands with two coordination modes, both of which assume a nearly planar geometry, serve as chelating bridges to ligate three Mn^{II} ions and thus result in two kinds of planar "$[Mn_3L]$" trinuclear motifs (Mn···Mn distances, average 6.3 Å; Scheme 2b). Then each trinuclear motif rivets with three nearest neighbors, and the adjacent triangles share only one lattice point, generating a 2D structure with a wavy Kagomé lattice (Figure 2a,b). A closer examination reveals that the phen ligands intrude into the cavities in **1**, resulting in interdigitation of the 2D networks, and the interdigitated phen rings form $\pi-\pi$ stacking with four different phen rings from the adjacent layers, with a centroid-to-centroid distance of ca. 4.16 Å (the shortest distance between interdigitated phen rings is 3.77 Å; see Figure S3 in the Supporting Information). In addition, there exist some hydrogen-bonding interactions arising from the proton on the coordinated O atoms of the $TzDC^{3-}$ ligands and the enclathrated solvent water molecules.

For **1**, a more interesting feature is that the chiral structure of the Kagomé lattice is obtained through spontaneous resolution.[11,12] Although the H_3TzDC and phen ligands are achiral, which act as a tris(bidentate) and a bidentate, respectively, in the process of crystallization, the metal ions may be fixed in chiral conformation. Consequently, the chirality of the three metal ions are seized by the rigid planar $TzDC^{3-}$ ligand, and the chirality is transferred to the 2D structure due to a corner-sharing Kagomé lattice. Finally,

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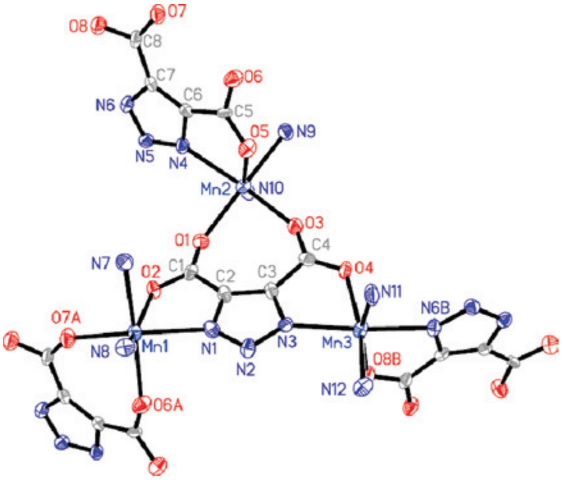

Figure 3. view of the coordination sphere in complex **2** (the C atoms of bipy are omitted for clarity). Selected bond distances (Å) and angles (deg): Mn1−O2 2.220(3), Mn1−O6A 2.149(4), Mn2−N4 2.265(4), Mn2−O1 2.164(4), Mn3−O8B 2.190(3), Mn3−N11 2.247(4); O2−Mn1−N1 72.5(1), N8−Mn1−N7 70.8(1), O3−Mn2−O1 89.4(1), O3−Mn2−N10 99.3(2), C8−O8−Mn3C 118.9(3), C8−O7−Mn1D 140.2(3). Symmetry codes: A, *x*, *y* + 1, *z*; B, −*x*, −*y*, *z* + ½; C, −*x*, −*y*, *z* − ½; D, *x*, *y* − 1, *z*.

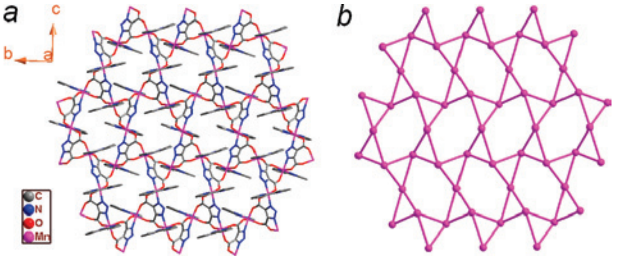

Figure 4. (a) 2D sheet along the *bc* plane in **2**. (b) Kagomé lattice (each Mn atom as a node) in complex **2**.

the extended chiral $\pi-\pi$ interactions of the phen ligands from different layers allow the chirality extended to the higher dimension, and hence such sheets stack along the *b* axis to form a chiral crystal of **1** and spontaneous resolution occurs with a generated conglomerate.

Complex **2** is isostructural with **1**, but it crystallizes in the acentric space group *Pca*2₁. [Crystal data **2**: $C_{38}H_{32}N_{12}Mn_3O_{12}$, $M_r = 1013.58$, orthorhombic, space group $Pca2_1$, $a = 19.2126(3)$ Å, $b = 9.9381(2)$ Å, $c = 21.4194(4)$ Å, $V = 4089.75(13)$ Å^3, $T = 293$ K, $Z = 4$, μ(Mo Kα) = 0.992 mm^{-1}, 45 545 reflections measured, 8769 unique (R_{int} = 0.0971), R1 = 0.0389, wR2 = 0.0763 (all data), Flack value = 0.251(16). CCDC 676345 for **2**. The powder X-ray diffraction pattern for **2** is shown in Figure S2 in the Supporting Information.] In **2**, each Mn center is coordinated with a bipy ligand and two different TzDC^{3-} ligands, resulting in a 2D Kagomé lattice (Figure 3) parallel to the *bc* plane (Figure 4a,b). The Mn^{II} centers in the same layer are also chiral, but the adjacent layers have opposite handedness. Although the chiral metal centers are related by a 2-fold screw axis and hence the 2D Kagomé layer is chiral, the neighboring layers are related by two glide planes (in the *b* and *a* directions) and then the chirality is annihilated; complex **2** is therefore a racemate in the 3D sense. There also exist some hydrogen-bonding interactions and $\pi-\pi$ stacking from different 2,2′-bipyridine rings from the adjacent layers.

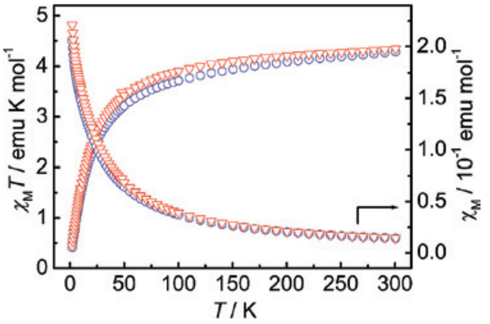

Figure 5. $\chi_M T$ vs T and χ_M vs T plots for **1** (○, blue) and **2** (▽, red).

The magnetic susceptibilities of complexes **1** and **2** were measured in the 2−300 K temperature range (Figure 5). At 300 K, the experimental $\chi_M T$ values of **1** and **2** are 4.28 and 4.33 emu mol^{-1} K, respectively, somewhat lower than the spin-only value (4.38 emu mol^{-1} K) expected for uncoupled high-spin Mn^{II} ions. Upon cooling, the $\chi_M T$ products decrease monotonically, while the χ_M values increase continuously. The data obey the Curie−Weiss law in the whole temperature range, with the Curie and Weiss constants being $C = 4.54$ emu mol^{-1} K and $\theta = -20.70$ K for **1** and $C = 4.60$ emu mol^{-1} K and $\theta = -18.17$ K for **2**. These features indicate apparent AF interactions between Mn^{II} ions in the two complexes. Because of the lack of an appropriate susceptibility expression for the 2D Kagomé system to simulate the experimental data, we are unable to evaluate interaction parameters.

It is well-established that magnetic frustration can suppress or significantly reduce long-range ordering. Experimentally, the degree of frustration is identified by the ratio of the Weiss constant to the ordering temperature, $f = |\theta|/T_N$.[9,13] For a nonfrustrated AF lattice, typical values of the ratio usually lie in the range of 2 to 4 or 5. For a frustrated system, the ratio is usually much larger. It is noted that complexes **1** and **2**, with θ values being about −20 K, do not show any indication of long-range ordering down to 2 K, suggesting that the ratios are larger than 10. This is consistent with the presence of frustration in the distorted Kagomé lattice.

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Supporting Information Available: X-ray crystallographic data in CIF format and experimental details, crystallographic data, selected bond lengths and angles, simulated and experimental powder X-ray diffraction patterns, and structures of $\pi-\pi$ stacking. This material is available free of charge via the Internet at http://pubs.acs.org.

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