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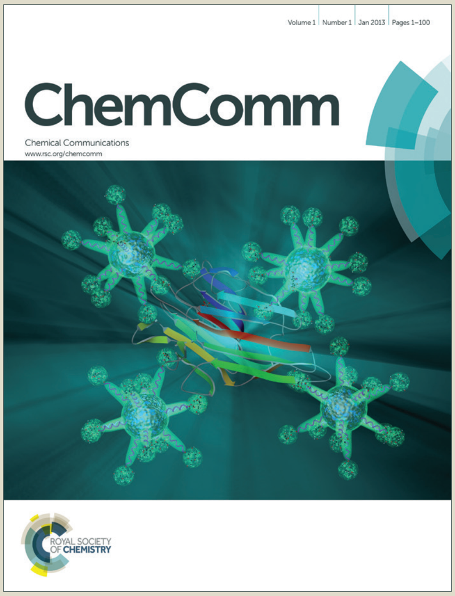

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Cite this: DOI: 10.1039/c1sc00000x

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ARTICLE TYPE

A Three Dimensional Magnetically Frustrated Metal-Organic Framework *via* Vertices Augmentation of Underlying Net

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Received (in XXX, XXX) Xth XXXXXXXXX 201X, Accepted Xth XXXXXXXXX 201X

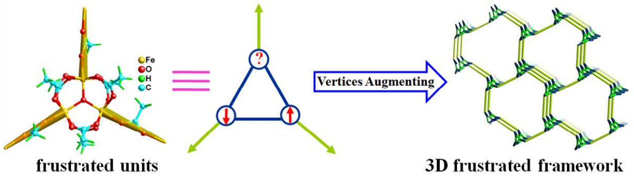
DOI: 10.1039/b000000x

In our efforts to fabricate magnetically frustrated materials, a feasible vertices augmentation method was used succesfully to construct a 4-fold interpenetrating three dimensional metal-organic framework (MOF) with rare *eta-c4* topology by linking $[Fe_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6]^+$ triangular moieties through the pure *anti, anti* acetate ligands. Strong antiferromagnetic interactions were found to exist between the neighboring Fe^{III} ions without long-range magnetic ordering above 2 K, indicating strong geometric spin frustration nature of this MOF.

Geometrically spin-frustrated systems have received considerable attention in the area of magnetism and condensed matter physics, as they can render the magnetic systems with various exotic properties, such as spin ice, spin liquids, spin glasses, high-*Tc* superconductivity, and monopoles in spin,[1-3] which makes the fabrication of frustration system an attractive goal in this active field.[4] To date, most geometrically frustrated systems can be conveniently identified through topology considerations based on the well-established structure databases.[6c] However, the rational design of novel geometrically frustrated systems is still a challenge due to the uncertainty of the assembly process that constrain the feasibility of arranging the spin-carriers in an artificial manner.[5]

In recent years, low-dimensional spin-frustrated inorganic compounds has been well explored and strategies for targeted construction have been developed.[5,6] At the same time, some unique molecule-based frustrated magnetic materials have also been obtained.[7] Nevertheless, compared with the broadly explored low-dimensional spin-frustrated lattices such as triangular and Kagomé lattice, the effective creation of three-dimensional (3D) frustrated systems is still a challenging task to researchers so far.[2,8] To achieve this goal, new design and construction strategies are urgently required.

Among the various potential frustrated magnetic materials, metal-organic frameworks (MOFs) show unique advantages in structure modulation since a desired complicated structure composed of simple underlying nets could be constructed by following a reverse engineering process.[9] Based on this heuristic work, we contend that 3D magnetically frustrated framework could be built from underlying nets with vertices as frustration units. However, structural match between basic units and the underlying network structure as well as the proper connections between spin centers needs to be considered simultaneously to realize the construction of materials with desired structures and properties. In the following study, we will corroborate that this method works well and should be generally applicable for coordination-based systems.



Scheme 1. The 3D frustrated framework via vertices augmentation of underlying net.

Herein, we report the successful construction of a magnetically frustrated MOF, $[NH_4]_2[Fe_9(\mu_3\text{-}O)_3(\mu\text{-}OAc)_{22}(H_2O)\cdot OAc]$ (**1**) (OAc = acetate), with triangular moiety $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6]^+$ cations as frustrated units[10] and acetate as linkers between the units. This MOF exhibits a 4-fold interpenetrating 3D framework structure with rare ***eta-c4*** topology. More importantly, strong antiferromagnetic interactions were observed between the Fe^{III} ions without long-range magnetic ordering above 2 K, indicating a strong geometric spin frustration nature of this MOF as expected.

1 was synthesized from the solvothermal reaction of $FeCl_3\cdot6H_2O$ in HOAc with urea saturation (Fig S1-S3). As depicted in Fig. S4, there are two different types of the triangular cluster $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6]^+$ involved in the asymmetric unit of **1** (denoted hereafter as type I and type II triangle for clarity), together with two acetate ligands in the *anti,anti* mode, one ammonium cation as well as one coordinated water. Obviously, type I triangular cluster is a μ_3-oxo-bridged trinuclear cluster containing three iron ions (Fe1, Fe2 and Fe3) in equivalent coordination environments. Each iron ion adopts a distorted-octahedral coordination geometry and accomplished by the

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†*Electronic supplementary information* (ESI) available: Additional crystallographic and magnetic data. For *ESI and crystallographic data in CIF or other electronic format see: DOI:*

central μ_3-O atom, four equatorial O centering from four *syn,syn* acetate anions, and one oxygen atom belonging to an *anti,anti* acetate ligand. On the other hand, the same coordination situation only holds for two iron ions (Fe4, Fe4^{ii}) of type II triangle, while the remaining Fe5 is coordinated by the central μ_3-O atom, four equatorial O from four *syn,syn* acetate ligands, and one terminal water molecule. Two uncoordinated acetate anions with part occupancy were also found in the space of the lattice. The Fe-O distances in **1** are all in the range of 1.896(5)-2.073 (11) Å (Table S1), and the Bond Valence model gives 3.029, 3.115, 3.147, 3.082 and 3.028 for Fe1 to Fe5, respectively. These results indicates that all the iron ions in **1** are trivalent.[11] To further confirm the valence state of Fe ions in bulk sample, UV-vis spectrum of **1** was investigated (Fig. S5). The intense absorption peak of the bulk sample appears around 200 nm, while the characteristic bands for the intervalence charge-transfer in mixed-valence iron (II,III) complexes are thoroughly absent in the region of 520~800 nm, indicating the uniform trivalent state of the Fe ions.[12]

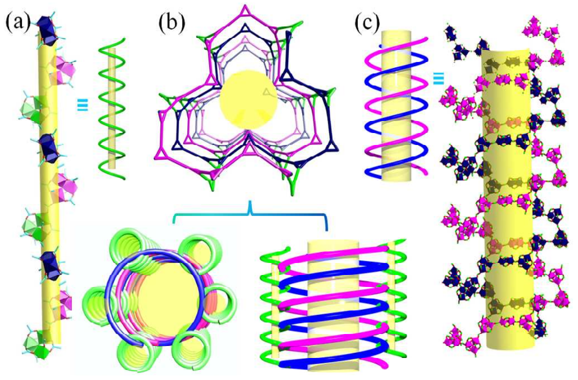

Fig. 1 (a) The single helix in **1**. (b) The linkage of the two types of helix structure. (c) The double helix structure in **1**.

In **1**, the neighboring triangular clusters are bridged by the same *anti,anti* acetate ligands but in different manners. For instance, the acetate ligand containing O3 and O4 serves as a bridge between different types of triangles (i.e., those associated with Fe3 and Fe4 ions, respectively), while the one having O13 and O14 links only two type I clusters through the coordination bonds Fe1-O14 and Fe2-O13^{i}. In this way, each type I triangular cluster is coupled to three of its neighbors, including two type I and one type II triangles, and the type II cluster bridges only two non-adjacent type I triangles. Following this linkage pattern, a single helix was generated by linking the type I triangles (Fig. 1a), and the type II cluster serves as a bridge linking six neighboring single helices, see Fig. 1b. Consequently, that will lead to the growth of a double helix chain structure as presented in Fig. 1c. It is worth noticing that all the double helices in **1** are of the same handedness in opposite to that of the single helices. This feature plays a key role in the formation of the interpenetrating 3D net structure presented in Fig. 2a, as it allows the linkage between different types of helices (Fig. 2b). It is amazed that there are 43-membered and 20-membered ring channels present in the current framework, along the *c* and [110] (or [100]) direction, respectively (Fig. S6). While the channels (defined by rings) containing 8-, 10-, and 12-membered rings are often found in zeotype inorganic structures, the complex with extra-large pores (>12-membered rings) has been sporadic.[13] The presence of 20-membered and 43-membered ring structure in **1** indicate that the proposed vertices augmentation strategy would be an effective way to obtain the structure containing large ring channels. In the context of topological structure, the type I triangle is a 3-connected node upon which an ***eta*** net framework can be built by following the pattern illustrated in Fig. 2b.[14] It is interesting to compare the structure of **1** and "star" lattice constructed by the same triangular entity.[10b] In the "star" lattice the isolated triangular building blocks serve as templates to make all of the triangular moieties in the "star" net coplanar. In **1** the whole ***eta*** framework is an anionic net, where each involved ammonium cation acts as a charge-balancer, and the neighbor triangular moieties bridged by *anti,anti* acetates have angles from 68.5º to 115.0º. All these ammonium cations are stabilized by the hydrogen bonds contributed by the oxygen atoms of the carboxylate ligands from two individual ***eta*** nets (Fig. S7). Based on aforementioned linkage, a 4-fold interpenetrating ***eta-c4*** net can then be conveniently established as demonstrated in Fig. 2c. It should be noted that the interpenetrating structure is very scarce in the presence of pure short-bridging ligands, which implies the key role of long-bridging ligands in the formation of interpenetrating structures. In this work, despite the use of short acetate ligands, the bridge moiety consisting of one type II triangle and two coordinated *anti,anti* acetate ligands could be considered as long-bridging metalloligands which contributes significantly to the formation of interpenetrating 3D framework. Furthermore, though this MOF is highly interpenetrated, reveals a relatively free volume of 20.4% per cell evaluated by PLATON analysis (Fig. 3d),[15] but shows poor performance on gas adsorption (i.e., 16.82 cm^3/g for CO_2 at 273 K and 1 bar). This might be attributed to the considerable relaxation of the interpenetrated framework after the removal of guest molecules which reduced its porsity.[16]

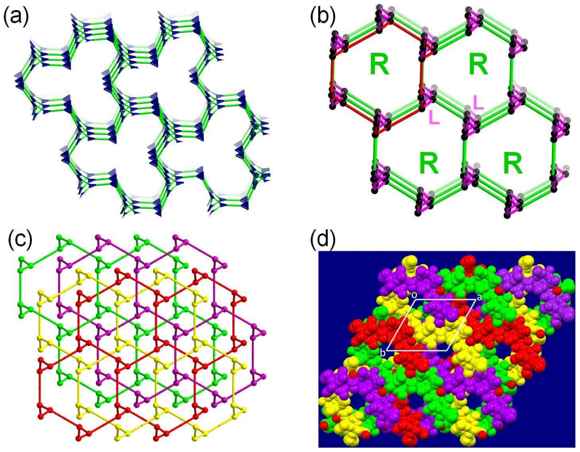

Fig. 2 (a) The predigested 3D iron triangular net of **1**. The $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAC)_6]^+$ clusters simplified as triangles and the acetate anions linking the triangles as green sticks. (b) The ***eta*** net with the triangles as single nodes showing the left-/right-handed helices. (c) View of the 4-fold interpenetrating ***eta*** net. (d) Spacefilling view of the 4-fold interpenetrating framework in **1**.

On the other hand, the structure of **1** promised it potential to exhibit frustrated magnetic properties. Neglecting the magnetic interactions between the four interpenetrating nets leads **1** to be a 3D magnetic net of $\{3;20;21\}_2\{3;20_2\}_6\{3\}$, where each Fe^{III} ion (except Fe5) interacts with three neighbors. Further ignoring Fe5 ions in **1** result in a new magnetic net of $\{20\}\{3;20^2\}_3$ with 40-number metal ions ring, where every two adjacent Fe3 ions on the same ring are linked to each other through two antiferromagnetically coupled Fe4 ions. Since the magnetic interaction between Fe3 and Fe4 ions is also antiferromagnetic, the neighboring Fe3 ions should be considered to be antiferromagnetically coupled to the net. Based on the aforementioned points, an ideal 3D frustrated magnetic net can be established by Fe1, Fe2, and Fe3 with point symbol of $\{3;16^2\}$ (Fig. S8).[14]

Magnetic properties of **1** were further investigated to confirm the frustrated nature of this MOF. Magnetic dc susceptibility of **1** was measured on the crystallized powder samples in an applied dc field of 0.1 T. As shown in Fig. 3, the result reveals the temperature dependence of the inverse molar magnetic susceptibility of **1**, ranging from 2 to 300 K. According to the inset, the value of $\chi_M T$ at 300 K is only 11.57 cm^3 mol^{-1} K, which is much smaller than that reported in the spin-only system. Therein, the value of $\chi_M T$ at 300 K is 39.36 cm^3 mol^{-1} K when considering nine fully spin-decoupled Fe^{III} ions with a magnetic spin of S = 5/2.[17] This discrepancy should be attributed to the significant antiferromagnetic couplings between the three high-spin Fe^{III} ions linked through the oxo bridges. Furthermore, the plot of $1/\chi_M$ *vs.* T in the range of 90-300K can be well fitted to the Curie–Weiss law with the Curie constant C =32.64 cm^3 mol^{-1} K and the Weiss temperature θ = -551.21 K. Thus, the effective magnetic moment μ_{eff} is 5.31 μ_B per Fe^{III} ion, which is much smaller than the one expected for high spin d^5 Fe^{III} ion (5.92 μ_B per Fe^{III} ion). The prominent reduction of μ_{eff} and the relatively large negative value for θ both support the presence of strong antiferromagnetic interactions in **1**.

It is notable that there is a "rebound" behavior of the magnetic dc susceptibility of **1**: the $\chi_M T$ value decreases continuously with decreasing temperature to reach a minimum of 0.43 cm^3 mol^{-1} K at 2.4 K, but then increases with further cooling. In fact, the increase of $\chi_M T$ below 2.4 K is more evident at low external magnetic fields. A reliable explanation is that the odd number of metal centers prevents the total cancellation of the antiferromagnetically coupled spins and/or spin-canting induced by the Dzyaloshinsky–Moriya interactions. Furthermore, there is a little difference between the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibilities at very low temperatures (Fig. S9), suggesting that the irreversible temperature (T_N) between the ZFC and FC for **1** is comparatively low and very close to 2 K, at which both small coercive force and remnant magnetization can be found (Fig. S10). In light of the aforementioned, it can be concluded that the strong spin frustration is indeed present in **1** due to the trigonal arrangement of spins, which would lead to a dramatic suppression of the long-range magnetic ordering at a considerable temperature range. According to the prediction by the quantum many-body Heisenberg interaction theory, the geometric lattice-induced magnetic frustration can only be found in the system with half-odd-integer spins but otherwise in integer spin or mixed-spin complexes.[10,19] This is because that the half-odd-integer spins of **1** could yield the ground-state lattice-induced frustration that give rise to an extremely low antiferromagnetic phase transition temperature.

An alternative way to evaluate the magnetic spin frustration is also given here by introducing the so-called frustration index of $f = |\theta| / T_N$, with $f > 10$ being an indication of strong spin frustration effects.[18] From the above θ value and the T_N value of 2.2 K, a value of 250 for f is obtained. Compared the magnetism of **1** with the "star" complex $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3][Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_{7.5}]_2\cdot 7H_2O$,[10b] we found that although the Weiss constant -551 K in **1** was large than -581 K in the "star" net, but the coercive force, remnant magnetization and T_N was lower than that in the 2D complex. That led to larger f value 250 in **1** and indicated that a stronger spin frustration effect could be gained in a 3D framework.

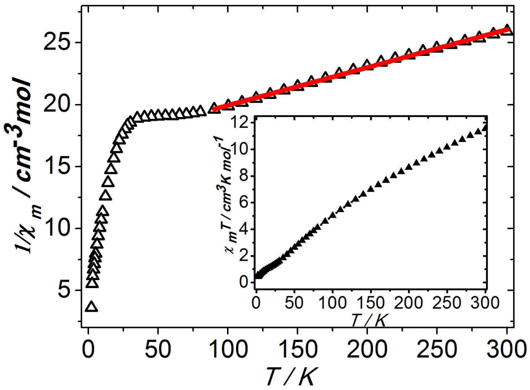

Fig. 3 The temperature dependence of the inverse molar magnetic susceptibility of **1** obtained in an applied dc field of 0.1 T; the solid line represents the behavior according to the Curie–Weiss law. Inset: The $\chi_M T$ vs. T plots of **1**.

In conclusion, an unprecedented 4-fold interpenetrating 3D framework was successfully constructed from the iron triangular clusters, with strong frustrated antiferromagnetic interactions achieved due to the triangular arrangement of spins. Thus, this work provides a promising and practical way to construct 3D magnetically frustrated MOFs, which is to augment the vertices of a simple underlying net with frustrated units. We believe this method might be generally applied to other coordination-driven systems. Moreover, it also sheds light on the investigation in the field of condensed matter physics, since the interpenetrating framework is not common for pure inorganic compounds but indeed feasible in the area of molecular materials.

Acknowledgements

This work was supported by the 973 Program of China (Grants 2014CB845600) and the NSF of China (Grants 21290171, 21471112 and 21421001) and MOE Innovation Team (IRT13022) of China.

Notes and references

[††]Synthesis of **1**: A mixture of $FeCl_3\cdot 6H_2O$ (5 mmol) and acetic acid solution 10 mL saturated with urea was sealed in a Teflon-lined stainless steel vessel, heated at 140 °C for 2 days under

autogenous pressure, and then cooled to room temperature. Red crystals of **1** were harvested in about ~30% yield based on $FeCl_3 \cdot 6H_2O$.

§Crystal data of **1,** $C_{46}H_{79}Fe_9N_2O_{50}$: M = 1962.76, Trigonal, space group $P3_221$, $a = b$ = 18.927(3) Å, c = 24.693(5) Å, Z = 3, ρ = 1.276 g/cm^3. Of 52932 total reflections collected, R_1 = 0.0518, wR_2 = 0.1474 and GOF = 1.089, Flack (x) = 0.137(8). CCDC 1042546 contains 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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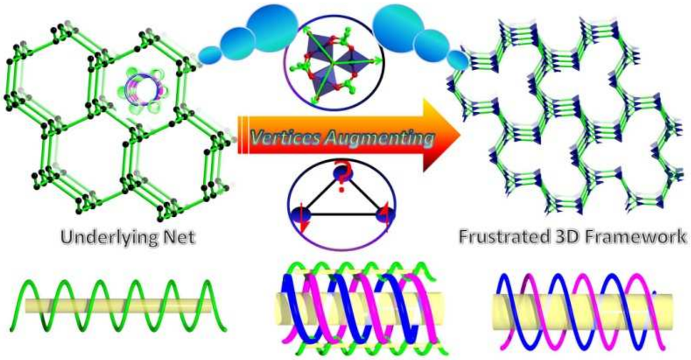
Synopsis

A Three Dimensional Magnetically Frustrated Metal-Organic Framework *via* Vertices Augmentation of Underlying Net

Jiong-Peng Zhao, Song-De Han, Xue Jiang, Jian Xu, Ze Chang, and Xian-He Bu*



A 3D magnetically frustrated metal-organic framework (MOF) was successfully designed and constructed from the augmentation on the vertices of a simple 3-connected underlying net. This MOF features unique interpenetrating framework structure and strong geometric spin frustration properties as expected.