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Communication

A Bilayer Triangular Lattice with Crown-like Co$_7$ Spin Cluster SBUs Exhibiting High Spin Frustration

Ya-Min Li,*[a] Hui-Jie Lun,[a] Chang-Yu Xiao,[a] Yan-Qing Xu,[b] Ling Wu,[c] Jing-He Yang,[a] Jing-Yang Niu[a] and Sheng-Chang Xiang*[c]

A novel bilayer metal-organic framework is assembled with perfect intralayer triangular subnet and ideal interlayer T$_d$ arrangement between unprecedented crown-like Co$_7$ cluster 10 units, exhibiting high spin frustration.

Recently geometrically frustrated antiferromagnet has been paid considerable attentions in solid state science, due to its great correlation with the ground-state behaviors such as spin liquids, spin ices and spin glasses.[1-3] Geometric spin frustration occurs 15 only when all nearest neighbor interactions can not be satisfied simultaneously, for example the triangular or the tetrahedral magnetic unit,[4] which is usually observed in individual or mixed corner- and/or edge-sharing magnetic lattices such as kagomé and triangular lattices in extended dimensional systems.[5,6] A lot of 20 investigations have been centered on the jarosite family of minerals.[7] Some frustrated magnets have also been reported on the basis of metal-organic frameworks containing the cluster units with odd nuclearity, such as trinuclear or pentanuclear clusters with antiferromagnetic couplings.[8] Among them, the examples 25 are comparatively common with triangular cluster units M$_3(\mu_3$-X) (M = transition metal ion, X = OH, O or F) positioned at kagomé or triangular lattice points and bridged by the ligands.[9] Besides, some zero-dimensional materials with the similar topological features as Kagomé and triangular lattices exhibit geometrical 30 frustration, for example Mn$^{III}_7$, Fe$^{III}_7$ disclike clusters and Fe$^{III}_{12}$ spin cluster, etc.,[10] which are expected to provide a deeper understanding of basic aspects of geometrical frustration.

Herein, we have achieved one highly frustrated 2D compound {[Co$_7$(OH)$_6$(1,4-npa)$_4$(H$_2$O)$_3$](dmt)$_{0.5}$·4H$_2$O}$_n$ (**1**) by the 35 hydrothermal reaction of CoCl$_2$·6H$_2$O, 1,4-npa and dmt (1,4-npa = 1,4-naphthalic acid, dmt = 2,4-diamine-6-methyl-triazine) (ESI†). The chemical formula is determined by elemental analysis. The structure is based on an unprecedented crown-like heptanuclear Co$_7$(OH)$_6$ spin cluster, which is firstly used as the 40 SBUs to display a beautiful bilayer 2D triangular lattice by the π-conjugated 1,4-npa bridges.

Compound **1** crystallized trigonal space group *R*–3 (ESI†), shows a 2D lattice consisting of {Co$_7$(OH)$_6$} cluster connected by 1,4-npa. As shown in Fig. 1a, it is observed that three 45 crystallographically distinct Co site within the heptanuclear cluster. All cobalt atoms are assigned as divalent cations and μ_3-O and μ_4-O atoms as hydroxyl oxygen atoms according to the charge balance and the BVS calculations.[11] On the Co(1) site, one

μ_3-OH, two μ_4-OH and three carboxyl-O atoms surround the Co 50 center in a slightly distorted octahedron. Co(2) atom also bears octahedral environment completed by one μ_4-OH, two μ_3-OH, two carboxyl-O atoms and one water molecule. A threefold axis passing through the Co(3) site, the Co(3) atom is therefore ligated by three μ_4-OH and three carboxyl-O atoms. Three μ_3-OH and 55 three μ_4-OH link Co(1), Co(2), Co(3) and the equivalents (Co(1A), Co(1B), Co(2A) and Co(2B)) (A: –y, –2+x–y, z; B: 2–x+y, –x, z) to crown-like heptanuclear cluster with the nearest Co…Co distance of about 2.9 Å (Fig. 1b). As far as we know, the reported {Co$_7$} complexes contain disclike or trigonal-prismatic 60 unit,[12] but crown-like heptanuclear cluster is unprecedented. Hydroxide groups bridging in μ_4 manner are displaced by 0.19 Å out of the best mean plane described by four Co^{II} atoms, which is unusual and few complexes involving transition metal ions are known.[13] Considering the Co–O–Co angles whose values dictate 65 the sign of the magnetic exchange coupling, it is established that the exchange coupling is antiferromagnetic for angles higher than 100° and ferromagnetic for lower values.[14] For the present case, the Co(2)–O(1)–Co(2), Co(3)–O(2)–Co(2) and Co(1)–O(2)–Co(1) angles of 141.6(2) °, 144.0(1) ° and 151.2(2) ° can be related to 70 antiferromagnetic coupling, as well as *syn, syn*-μ_2:η^1:η^1 carboxyl groups.
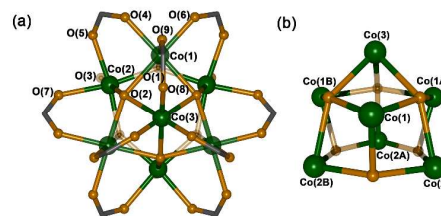

Fig. 1 (a) The coordination environment of the metal ions in **1**. (b) Crown-like Co$_7$(OH)$_6$ SBU of **1**. H atoms are omitted for clarity. 75 Symmetry codes: A: –y, –2+x–y, z; B: 2–x+y, –x, z. Color scheme: C, grey; Co, green and O, orange.

Each {Co$_7$(OH)$_6$} cluster as one SBU first connects other six adjacent SBUs by six linear 1,4-npa ligands to form one perfect 2D triangular sheet in the *ab* plane (Fig. 2a), and additionally 80 links three Co$_7$(OH)$_6$ by three other 1,4-npa further to form a double layer triangular network. Between double layer, the octahedral cages are formed by six Co$_7$(OH)$_6$ SBUs at the corners, and twelve 1,4-npa ligands at edges, as well as the ideal tetrahedral cages defined by four Co$_7$(OH)$_6$ SBUs at the corners, 85 and six 1,4-npa ligands at edges (Fig. 2b). The O$_h$–cage aperture

is approximately 5 Å and the open window of about 4×4 Å, and T_d–cage aperture of about 3 Å. Every O_h–cage is therefore surrounded by six T_d–cages, and the 2D network may be alternatively described as the formation by sharing the corners of O_h–cage and T_d–cage. From topological views, considering every $Co_7(OH)_6$ SBU as 9-connected node, and the ligand 1,4-npa as linker, the double layer 2D triangular frustrated framework may be also simplified as a uninodal nine-connected 2D network with schläfli symbol of $\{3^{15}.4^{18}.5^3\}$ (Fig. 2c). The perfect intralayer triangular lattice and ideal interlayer tetrahedral arrangement indicate geometrical frustration in **1**.[4] The experimental and simulated PXRD patterns agree well with each other (Fig. S2, ESI†), confirming the good phase purity. The thermogravimetric curve (Fig. S3, ESI†) shows high stability of compound **1**.
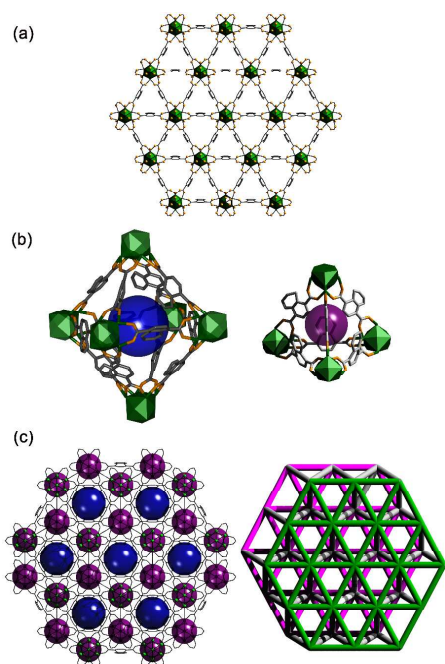

Fig. 2 (a) 2D triangular sheet of **1** viewed along the *c*-axis direction. (b) Octahedral and tetrahedral cages. (c) Double layer 2D triangular network of **1** viewed along the *c*-axis direction. Green polyhedrons represent $Co_7(OH)_6$ clusters. Blue and purple balls highlight voids inside cages and H atoms are omitted for clarity. Color scheme: C, grey; Co, green and O, orange.

The perfect triangular and tetrahedral frustrated connections of **1** drive us to explore the intermolecular magnetic couplings which might be propagated through the extended π-conjugated 1,4-npa bridges between heptanuclear Co^{II} clusters.[15] It was shown in Fig. 3 about the $\chi_m T$ *vs. T* and χ_m^{-1} *vs. T* plots of **1** in the range of 2–300 K at 1 kOe. The $\chi_m T$ value is 15.16 cm³ mol⁻¹ K at 300 K, lower than the spin-only value of seven high-spin non-interacting Co^{II} ions 20.5 cm³ mol⁻¹ K assuming $S_i = 3/2$ and a average *g* value of 2.5.[16] With the temperature lowered, the $\chi_m T$ value gradually decreases to reach the value of 1.07 cm³ mol⁻¹ K at 2 K, which shows antiferromagnetic behaviour. Unfortunately, no suitable model can be used to fit the magnetic data due to the complicated magnetic couplings in the 2D heptanuclear Co^{II} system of **1**. Fitting the temperature dependence of the reciprocal susceptibility (χ_m^{-1}) using the Curie-Weiss law in the temperature 300 K–25 K, yields large negative θ value (θ = –124.45 K) and *C* = 21.28 cm³ mol⁻¹ K, which also indicate strong antiferromagnetic interactions.
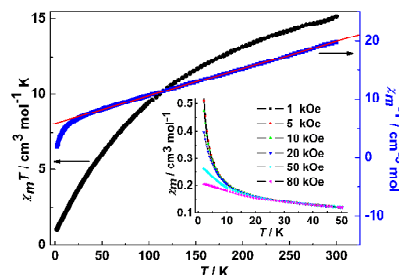

Fig. 3 The $\chi_m T$ *vs. T* and χ_m^{-1} *vs. T* plots of **1** in the range of 2–300 K at 1 kOe; the red solid line is the best-fit; inset: the χ_m *vs. T* plots of **1** in the range 2−50 K at different fields.

In order to check for magnetic behaviour at low temperatures, field-cooled magnetizations (FCM) and zero-field-cooled magnetizations (ZFCM) were measured at 100 Oe and 200 Oe (Fig. S4, ESI†). And it is observed that the curves are identical and no divergence occurs for ZFCM and FCM curves upon the same field, indicating there is no spontaneous magnetization down to 2 K. With the increasing external field, the curves of χ_m at 2–30 K under high field (1–80 kOe) show field-dependent decrease, but no sharp transition indicative of magnetic order appears, even down to 2 K, suggesting no antiferromagnetic long-range ordering occurs and the compound retains its traditional paramagnetic state above 2 K (T_N < 2 K) (Fig. 3 inset).[17]

The field dependence of the isothermal magnetization *M*(H) at 2 K was also measured (Fig. S5, ESI†), which doesn't show hysteresis but shows an increase with the field and reaches 2.66 *Nβ* at 80 kOe, a value that is far below the saturation value 16.8 *Nβ* expected for seven spin-only Co^{II} ions, which further confirms the antiferromagnetic interactions at low temperature. In addition, the ac susceptibilities in the range of 500–3000 Hz also indicate the above results. The *χ′* *vs. T* curves in a field of 3 Oe are analogous that no peaks above 2 K and no frequency dependence are observed (Fig. S6, ESI†), similar to the literature reported.[17c]

The observed strong antiferromagnetism may be understood by intramolecular and intermolecular magnetic exchange pathways. Within heptanuclear Co^{II} units, although the angles Co(1)–O(2)–Co(3) (84.8(1) °), Co(1)–O(2)–Co(2) (86.4(1) °) and Co(2)–O(1)–Co(1) (94.1(1) °) define ferromagnetic interactions, Co(2)–O(1)–Co(2) (141.6(2) °), Co(3)–O(2)–Co(2) (144.0(0) °) and Co(1)–O(2)–Co(1) (151.2(2) °) indicate more strong antiferromagnetic interactions,[14] as well as *syn, syn*–carboxylate bridges serving to the antiferromagnetic interactions.[18] Meanwhile, the π-conjugated 1,4-npa bridge provides intermolecular antiferromagnetic coupling between Co_7 clusters.[15] The magnetic data also suggest an important spin-frustrated behaviour of **1**. Ramirez has provided a measure for spin frustration by defining $f = |\theta/T_N|$ with value of *f* > 10 signifying a strong effect,[4a,19] According to the definition, **1** shows high spin frustration, with the value of *f* > 63.2. As far as we know, only few cases such as $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3][Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_{7.5}]_2·7H_2O$ and $ZnCu_3(OH)_6Cl_2$ bear a large *f* value.[8b,17a] However, the *f* values cannot be compared directly between the compounds of isotropic ions such as Fe^{III} and anisotropic Co^{II} ions. The high frustration for **1** may be interpretative as below: (a) **1** has odd heptanuclear $Co_7(OH)_6$

cluster units. The Co_7 cluster can be looked as a polyhedron consisting of eleven triangular faces (Fig. S7, ESI†), of which the frustrated magnetic interactions are dominated by the arrangement of spins on the triangular faces. (b) The trigonal space group $R-3$ brings the double layer structure of **1** with both its intra-layer triangular subnet and its inter-layer T_d arrangement between the Co_7 cluster SBUs perfectly frustrated.

In conclusion, we firstly report a novel bilayer triangular lattice with the unique crown-like $Co_7(OH)_6$ cluster SBUs, which contains the perfect intra-layer triangular network and ideal inter-layer T_d arrangement. Compound **1** presents the first example of the bilayer triangular lattice with high frustration. It offers an opportunity for spin frustrated realization on molecular level, meanwhile provides a deeper understanding of basic aspects of geometrical frustration in the extended π-conjugated system.

Notes and references

a Henan Key Laboratory of Polyoxometalate; Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan, 475004, China; E-mail: liyamin@henu.edu.cn

b School of Chemistry, Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Institute of Technology, Beijing, 100081, China

c Fujian Provincial Key Laboratory of Polymer Materials, College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou, Fujian, 350007, China; E-mail: scxiang@fjnu.edu.cn

† Electronic Supplementary Information (ESI) available: experimental, crystallographical and physical characterization sections, additional graphics (Fig. S1–Fig. S7) and tables for **1** (Table S1–Table S3). CCDC reference number 982028. For ESI and crystallographic data in CIF see DOI: 10.1039/b000000x/

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