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

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 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. Geometric spin frustration occurs only when all nearest neighbor interactions can not be satisfied simultaneously, for example the triangular or the tetrahedral magnetic unit, 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. A lot of investigations have been centered on the jarosite family of minerals. 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. Among them, the examples are comparatively common with triangular cluster units M$_3$(µ$_3$-X) $(M = transition metal ion, X = OH, O or F)$ positioned at kagomé or triangular lattice points and bridged by the ligands. Besides, some zero-dimensional materials with the similar topological features as Kagomé and triangular lattices exhibit geometrical frustration, for example Mn$_{11}^{11}$, Fe$_{12}^{12}$, disclike clusters and Fe$_{12}^{12}$ spin cluster, etc., 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)$_3$(H$_2$O)$_3$}($dmt$)$_4$·4H$_2$O]$_n$ (I) by the 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 SBUs to display a beautiful bilayer 2D triangular lattice by the π-conjugated 1,4-npa bridges.

Compound I 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 crystallographically distinct Co site within the heptanuclear cluster. All cobalt are assigned as divalent cations and µ$_3$-O and µ$_5$-O atoms as hydroxyl oxygen atoms according to the charge balance and the BVS calculations. On the Co(I) site, one µ$_3$-OH, two µ$_2$-OH and three carboxyl-O atoms surround the Co center in a slightly distorted octahedron. Co(2) atom also bears octahedral environment completed by one µ$_2$-OH, two µ$_2$-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$_3$-OH and three carboxyl-O atoms. Three µ$_3$-OH and three µ$_2$-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, z, −x) 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 unit, but crown-like heptanuclear cluster is unprecedented. Hydroxide groups bridging in µ$_3$ manner are displaced by 0.19 Å out of the best mean plane described by four Co$_7$ clusters, which is unusual and few complexes involving transition metal ions are known. Considering the Co–O–Co angles whose values dictate 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. 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 antiferromagnetic coupling, as well as syn, syn-µ$_2$η$^6$-η$^1$ carboxyl groups.

![Fig. 1](https://example.com/fig1.png)

Fig. 1 (a) The coordination environment of the metal ions in I. (b) Crown-like Co$_7$(OH)$_6$ SBU of I. H atoms are omitted for clarity. Symmetry codes: A: −x−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 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, 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 T₆-cage aperture of about 3 Å. Every O₆-cage is therefore surrounded by six T₆-cages, and the 2D network may be alternatively described as the formation by sharing the corners of O₆-cage and T₆-cage. From topological views, considering every Co₆(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 unimodal nine-connected 2D network with schläfli symbol of \{3\15.4\18.5\} (Fig. 2c). The perfect intralayer triangular lattice and ideal interlayer tetrahedral arrangement indicate geometrical frustration in 1. 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.

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 Co₇ clusters.\(^{15}\) It was shown in Fig. 3 about the \(\chi_m T\) vs. \(T\) and \(\chi_m^{-1} vs. T\) 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 Co₇ ions 20.5 cm³ mol⁻¹ K assuming \(S = 3/2\) and an 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 Co₇ system of 1. Fitting the temperature dependence of the reciprocal susceptibility (\(\chi_m^{-1}\)) using the Curie-Weiss law in the temperature range 300 K–25 K, yields large negative \(\theta\) value (\(\theta = -124.45\) K) and \(C = 21.28\) cm³ mol⁻¹ K, which also indicate strong antiferromagnetic interactions.

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 \(\chi_m\) 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 \(\mu_B\) at 80 kOe, a value that is far below the saturation value 16.8 \(\mu_B\) 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 \(\chi'\) 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 Co₇ 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 Co₇ 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.\(^{19a}\) 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 [Fe₆(μ₃-O)(μ-OAc)₆(H₂O)₄][Fe₂(μ₃-O)(μ-OAc)₇]·7H₂O and ZnCu₃(OH)₆Cl₂ 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 Co₆(OH)₆...
cluster units. The Co$_7$ cluster can be looked as a polyhedron consisting of eleven triangular faces (Fig. S7, ES1), 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 $I$ with both its intra-layer triangular subnet and its inter-layer $T_4$ 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 $T_4$ arrangement. Compound $I$ 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 n-conjugated system.

The authors gratefully acknowledge the supports from Recruitment Program of Global Young Experts, Program for New Century Excellent Talents in University (NCET-10-0108), the Natural Science Foundation of China (21271025, 21273033), the Award ‘Minjiang Scholar Program’ in Fujian Province, the Department of Science and Technology of Henan Province (122102210174), the Natural Science Foundation of the Education Department of Henan Province (2011A150004, 12B150004) and the State Key Laboratory of Structural Chemistry (20110008). Great thanks to P.-T. Ma, L.-S. Wang, X.-D. Zhang and R.-B. Fu for their helps.

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