

# A bilayer triangular lattice with crown-like Co<sub>7</sub> spin cluster SBUs exhibiting high spin frustration†

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**A novel bilayer metal–organic framework is assembled with a perfect intralayer triangular subnet and ideal interlayer T<sub>d</sub> arrangement between unprecedented crown-like Co<sub>7</sub> cluster units, exhibiting high spin frustration.**

Recently geometrically frustrated antiferromagnets have been paid considerable attention in solid state science, due to their great correlation with ground-state behaviors such as spin liquids, spin ices and spin glasses.<sup>1–3</sup> Geometric spin frustration occurs only when all nearest neighbor interactions can not be satisfied simultaneously, for example in a triangular or tetrahedral magnetic unit,<sup>4</sup> 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.<sup>5,6</sup> A lot of investigations have centered on the jarosite family of minerals.<sup>7</sup> Some frustrated magnets have also been reported on the basis of metal–organic frameworks containing cluster units with odd nuclearity, such as trinuclear or pentanuclear clusters with antiferromagnetic couplings.<sup>8</sup> Among these, the examples are comparatively common with triangular cluster units M<sub>3</sub>(μ<sub>3</sub>-X) (M = transition metal ion, X = OH, O or F) positioned at kagomé or triangular lattice points and bridged by ligands.<sup>9</sup> Also, some zero-dimensional materials with similar topological features as kagomé and triangular lattices exhibit geometrical frustration, for example Mn<sup>III</sup><sub>7</sub>, Fe<sup>III</sup><sub>7</sub> disc-like clusters and Fe<sup>III</sup><sub>12</sub> spin cluster, *etc.*,<sup>10</sup> which are expected to provide a deeper understanding of basic aspects of geometrical frustration.

Herein, we have achieved one highly frustrated 2D compound  $\{[\text{Co}_7(\text{OH})_6(1,4\text{-npa})_4(\text{H}_2\text{O})_3](\text{dmt})_{0.5}\cdot 4\text{H}_2\text{O}\}_n$  (**1**) by hydrothermal reaction of CoCl<sub>2</sub>·6H<sub>2</sub>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<sub>7</sub>(OH)<sub>6</sub> spin cluster, which is firstly used as the SBU (secondary building unit) to display a bilayer 2D triangular lattice with π-conjugated 1,4-npa bridges.

Compound **1** crystallized to trigonal space group R $\bar{3}$  (ESI†), and shows a 2D lattice consisting of {Co<sub>7</sub>(OH)<sub>6</sub>} clusters connected by 1,4-npa. As shown in Fig. 1a, it is observed that there are three crystallographically distinct Co sites within the heptanuclear cluster. All cobalt atoms are assigned as divalent cations, and μ<sub>3</sub>-O and μ<sub>4</sub>-O atoms as hydroxyl oxygen atoms according to the charge balance and the BVS (bond valence sums) calculations.<sup>11</sup> On the Co(1) site, one μ<sub>3</sub>-OH, two μ<sub>4</sub>-OH and three carboxyl-O atoms surround the Co center in a slightly distorted octahedron. The Co(2) atom also bears an octahedral environment formed of one μ<sub>4</sub>-OH, two μ<sub>3</sub>-OH, two carboxyl-O atoms and one water molecule. A threefold axis passes through the Co(3) site, the Co(3) atom is therefore ligated by three μ<sub>4</sub>-OH and three carboxyl-O atoms. Three μ<sub>3</sub>-OH and three μ<sub>4</sub>-OH link Co(1), Co(2), Co(3) and their equivalents (Co(1A), Co(1B), Co(2A) and Co(2B)) (A: -y, -2 + x - y, z; B: 2 - x + y, -x, z) in a crown-like heptanuclear cluster with the nearest Co···Co distance of about 2.9 Å (Fig. 1b). As far as we know, reported {Co<sub>7</sub>} complexes also

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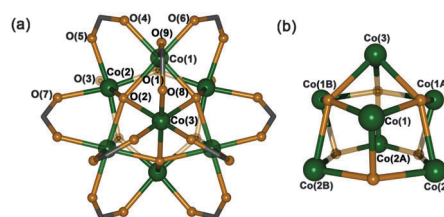


Fig. 1 (a) The coordination environment of the metal ions in **1**. (b) Crown-like Co<sub>7</sub>(OH)<sub>6</sub> SBU of **1**. H atoms are omitted for clarity. Symmetry codes: A: -y, -2 + x - y, z; B: 2 - x + y, -x, z. Color scheme: C, grey; Co, green; and O, orange.

contain a disc-like or trigonal-prismatic unit,<sup>12</sup> but a crown-like heptanuclear cluster is unprecedented. Hydroxide groups bridging in a  $\mu_4$  manner are displaced by 0.19 Å out of the best mean plane described by four Co<sup>II</sup> atoms, which is unusual and few complexes involving transition metal ions are known.<sup>13</sup> 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.<sup>14</sup> 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- $\mu_2$ : $\eta^1$ : $\eta^1$*  carboxyl groups.

Each {Co<sub>7</sub>(OH)<sub>6</sub>} cluster as one SBU first connects to the 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 then additionally links three Co<sub>7</sub>(OH)<sub>6</sub> by three other 1,4-*npa* to form a double layer triangular network. Between the double layer, the octahedral cages are formed by six Co<sub>7</sub>(OH)<sub>6</sub> SBUs at the corners, and twelve 1,4-*npa* ligands at the edges, as well as the ideal tetrahedral cages defined by four Co<sub>7</sub>(OH)<sub>6</sub> SBUs at the corners, and six 1,4-*npa* ligands at the edges (Fig. 2b). The O<sub>h</sub>-cage aperture is approximately 5 Å and the open window of about 4 × 4 Å, and T<sub>d</sub>-cage aperture of about 3 Å. Every O<sub>h</sub>-cage is therefore surrounded by six T<sub>d</sub>-cages, and the 2D network may be alternatively described by the formation of O<sub>h</sub>-cage and T<sub>d</sub>-cage shared corners. From topological views, considering every Co<sub>7</sub>(OH)<sub>6</sub> 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<sup>15</sup>.4<sup>18</sup>.5<sup>3</sup>} (Fig. 2c). The perfect intralayer

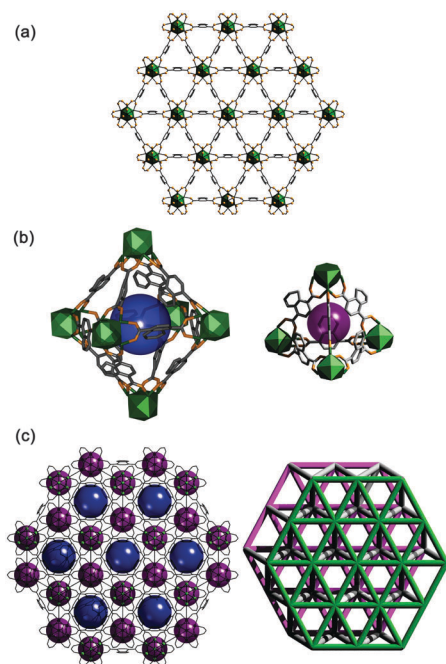


Fig. 2 (a) 2D triangular sheet of **1** viewed along the *c*-axis direction. (b) Octahedral and tetrahedral cages. (c) Double layer 2D triangular network of **1** viewed along the *c*-axis direction. Green polyhedrons represent Co<sub>7</sub>(OH)<sub>6</sub> clusters. Blue and purple balls highlight voids inside cages and H atoms are omitted for clarity. Color scheme: C, grey; Co, green and O, orange.

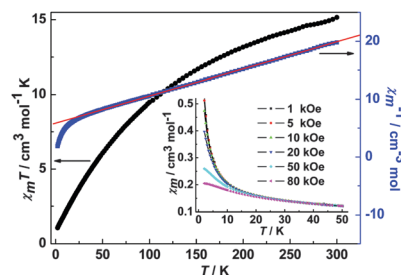


Fig. 3 The  $\chi_m T$  vs.  $T$  and  $\chi_m^{-1}$  vs.  $T$  plots of **1** in the range of 2–300 K at 1 kOe; the red solid line is the best-fit; inset: the  $\chi_m$  vs.  $T$  plots of **1** in the range 2–50 K in different fields.

triangular lattice and ideal interlayer tetrahedral arrangement indicate geometrical frustration in **1**.<sup>4</sup> The experimental and simulated PXRD patterns agree well with each other (Fig. S2, ESI<sup>†</sup>), confirming the good phase purity. The thermogravimetric curve (Fig. S3, ESI<sup>†</sup>) 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  $\pi$ -conjugated 1,4-*npa* bridges between heptanuclear Co<sup>II</sup> clusters.<sup>15</sup> Fig. 3 shows 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 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K, lower than the spin-only value of seven high-spin non-interacting Co<sup>II</sup> ions at 20.5 cm<sup>3</sup> mol<sup>-1</sup> K assuming  $S_i = 3/2$  and an average  $g$  value of 2.5.<sup>16</sup> With the temperature lowered, the  $\chi_m T$  value gradually decreases to reach the value of 1.07 cm<sup>3</sup> mol<sup>-1</sup> 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<sup>II</sup> system of **1**. Fitting the temperature dependence of the reciprocal susceptibility ( $\chi_m^{-1}$ ) using the Curie–Weiss law in the temperature 300–25 K, yields large negative  $\theta$  value ( $\theta = -124.45$  K) and  $C = 21.28$  cm<sup>3</sup> mol<sup>-1</sup> K, which also indicates 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<sup>†</sup>). It is observed that the curves are identical and no divergence occurs for ZFCM and FCM curves in 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).<sup>17</sup>

The field dependence of the isothermal magnetization  $M(H)$  at 2 K was also measured (Fig. S5, ESI<sup>†</sup>), which does not show hysteresis but shows an increase with the field and reaches 2.66  $N\beta$  at 80 kOe, a value that is far below the saturation value 16.8  $N\beta$  expected for seven spin-only Co<sup>II</sup> 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 so that no peaks above 2 K and no frequency dependence are observed (Fig. S6, ESI<sup>†</sup>), similar to the reported literature.<sup>17c</sup>

The observed strong antiferromagnetism may be understood by intramolecular and intermolecular magnetic exchange pathways. Within heptanuclear  $\text{Co}^{\text{II}}$  units, although the angles  $\text{Co}(1)\text{-O}(2)\text{-Co}(3)$  ( $84.8(1)^\circ$ ),  $\text{Co}(1)\text{-O}(2)\text{-Co}(2)$  ( $86.4(1)^\circ$ ) and  $\text{Co}(2)\text{-O}(1)\text{-Co}(1)$  ( $94.1(1)^\circ$ ) define ferromagnetic interactions,  $\text{Co}(2)\text{-O}(1)\text{-Co}(2)$  ( $141.6(2)^\circ$ ),  $\text{Co}(3)\text{-O}(2)\text{-Co}(2)$  ( $144.0(0)^\circ$ ) and  $\text{Co}(1)\text{-O}(2)\text{-Co}(1)$  ( $151.2(2)^\circ$ ) indicate more strong antiferromagnetic interactions,<sup>14</sup> as well as *syn,syn*-carboxylate bridges serving the antiferromagnetic interactions.<sup>18</sup> Meanwhile, the  $\pi$ -conjugated 1,4-npa bridge provides intermolecular antiferromagnetic coupling between  $\text{Co}_7$  clusters.<sup>15</sup> The magnetic data also suggest an important spin-frustrated behaviour of **1**. Ramirez has provided a measure for spin frustration by defining  $f = |\theta/T_{\text{N}}|$  with value of  $f > 10$  signifying a strong effect.<sup>4a,19</sup> According to the definition, **1** shows high spin frustration, with the value of  $f > 63.2$ . As far as we know, only a few cases such as  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-OAc})_6(\text{H}_2\text{O})_3][\text{Fe}_3(\mu_3\text{-O})(\mu\text{-OAc})_{7.5}]_2 \cdot 7\text{H}_2\text{O}$  and  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$  bear a large  $f$  value.<sup>8b,17a</sup> However, the  $f$  values cannot be compared directly between the compounds of isotropic ions such as  $\text{Fe}^{\text{III}}$  and anisotropic  $\text{Co}^{\text{II}}$  ions. The high frustration for **1** may be interpreted as below: (a) **1** has odd heptanuclear  $\text{Co}_7(\text{OH})_6$  cluster units. The  $\text{Co}_7$  cluster can be considered to be a polyhedron consisting of eleven triangular faces (Fig. S7, ESI<sup>†</sup>), of which the frustrated magnetic interactions are dominated by the arrangement of spins on the triangular faces; (b) the trigonal space group  $R\bar{3}$  brings the double layer structure of **1** with both its intralayer triangular subnet and its inter-layer  $T_d$  arrangement between the  $\text{Co}_7$  cluster SBUs perfectly frustrated.

In conclusion, we first report a novel bilayer triangular lattice with unique crown-like  $\text{Co}_7(\text{OH})_6$  cluster SBUs, which contain a perfect intralayer 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 a molecular level, and provides a deeper understanding of basic aspects of geometrical frustration in extended  $\pi$ -conjugated systems.

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