Coexistence of spin frustration and long-range magnetic ordering in a triangular $Co^{II}_3(\mu_3\text{-OH})$-based two-dimensional compound†

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A two-dimensional compound $[Co_3(\mu_3\text{-OH})_2(1,2\text{-chdc})_2]_\infty$ (1,2-chdc = *trans*-1,2-cyclohexane-dicarboxylate) comprising triangular arrays of $Co^{II}_3(\mu_3\text{-OH})$ affording a Kagomé-like lattice exhibits the coexistence of spin frustration and long-range magnetic ordering.

Spin-frustration, defined as a system's inability to satisfy all antiferromagnetic interactions between spins simultaneously, amplifies the context of molecular-based magnets because they can lead to macroscopic degeneracies and qualitatively new states of matter.[1] Magnetic long-range ordering (LRO) may be suppressed or significantly reduced as a result of competing antiferromagnetic exchange interactions.[2,3] Spin-frustrated systems are ubiquitous, and they can be deliberately designed in certain topologies (ESI Scheme S1†), which are so-called geometrically frustrated lattices such as the triangular, Kagomé, pyrochlore and fcc lattices (ESI Scheme S2†),[1] whereas the true LRO is only limited in three-dimensional (3D) or two-dimensional (2D) Ising systems.[4] Combination of these two kinds of behaviour into a single crystal lattice might result in new physical properties. An attractive strategy for creating these "bi-functional" magnets targets inorganic–organic hybrid materials.[5] In this method, the inorganic components are mainly based on the assembly of triangular secondary building units including $M_3(\mu_3\text{-OH})$ (M = transition metal ion) moieties. So far the metal ions employed in the $M_3(\mu_3\text{-OH})$ triangles have been mainly $V^{II/III}$, $Cr^{II/III}$ and $Fe^{II/III}$.[6,7] In fact, Co^{II} ions can also form antiferromagnetically-coupled triangular $Co^{II}_3(\mu_3\text{-OH})$ moieties with versatile topologies,[8,9] particularly the novel Δ-chain,[8a] which represents a section of Kagomé lattice showing a whole 3D spin frustration and no magnetic ordering down to 2 K, therefore one would expect that triangular $Co^{II}_3(\mu_3\text{-OH})$ could also be used to assemble a 2D frustrated antiferromagnet. However, to our knowledge, no 2D cobalt(II) hydroxide with distinct spin frustration has been reported.

Inspired by the fact that succinic acid as an analogue of *trans*-1,2-cyclohexane-dicarboxylic acid (1,2-chdcH_2) was used to incorporate $Co^{II}_3(\mu_3\text{-OH})$ moieties into inorganic–organic hybrid materials,[10] we chose 1,2-chdcH_2 in the preparation of layered hybrid materials with the highly hydrophobic aliphatic component of 1,2-chdc for efficient separation of the magnetic exchange between the layers, and successfully generated a new organically sandwiched cobalt(II) hydroxide ${}^2_\infty[Co_3(\mu_3\text{-OH})_2(1,2\text{-chdc})_2]$ (**1**)‡ possessing a new geometrical topology analogous to the Kagomé lattice and showing the coexistence of spin frustration and long-range magnetic ordering.

In the crystal structure§ of **1** (Fig. 1), each asymmetrical unit contains three Co^{II} atoms, two μ_3-OH groups and two 1,2-chdc ligands. Co1 is in a distorted tetrahedral geometry with four oxygen atoms from two hydroxyl and two carboxylate ligands (Co–O 1.943(3)–2.093(3) Å; O–Co–O 97.8(1)–136.7(2)°), while

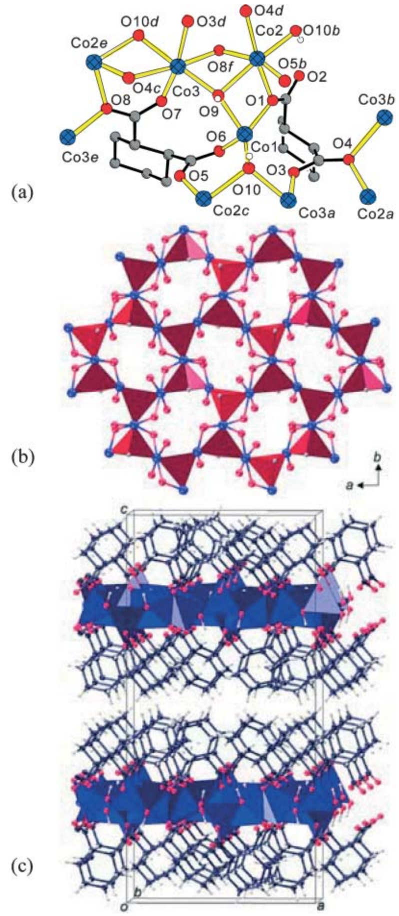

Fig. 1 Views of the metal–ligand environments (symmetric codes: $a = x + 0.5, y, -z + 0.5$; $b = -x + 1, y - 0.5, -z + 0.5$; $c = -x + 1, y + 0.5, -z + 0.5$; $d = x - 0.5, y, -z + 0.5$; $e = -x + 0.5, y + 0.5, z$; $f = -x + 0.5, y - 0.5, z$) (a), 2D Kagomé-like lattice (O atoms of μ_3-OH are highlighted in red polyhedra and the C atoms are omitted for clarity) (b), and packing diagram (Co atoms are highlighted in blue polyhedra) (c) in **1**.

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Co2 is in a slightly distorted octahedron with two *trans* μ_3-OH groups (Co–O 2.080(4)–2.135(3) Å; O–Co–O 172.2(1)°) and equatorial *cis* arrangement of carboxylate-*O* oxygen atoms (Co–O 2.073(4)–2.102(3) Å; O–Co–O 86.2(2)–96.4(2)°), and Co3 is coordinated in an elongated octahedron with the axial positions occupied by two carboxylate-*O* oxygen atoms (Co–O 2.209(3)–2.406(4) Å) and the equatorial positions by two carboxylate-*O* oxygen atoms and two μ_3-OH groups (Co–O 2.019(3)–2.142(4) Å) (Fig. 1a). The arrangement of metal ions is unusual. Co1, Co2 and Co3 are connected by two independent μ_3-OH groups, giving two kinds of triangles of $Co_1Co_2Co_3$ and $Co_1Co_{2c}Co_{3a}$, which are hereafter referred as Δ-(μ_3-O_9) and Δ-(μ_3-O_{10}), respectively. The mean Co–O bond length of Δ-(μ_3-O_9) is 2.084 Å, being slightly longer than that (2.014 Å) of Δ-(μ_3-O_{10}). Δ-(μ_3-O_9) is greatly deviated from an equilateral triangle (Co···Co 3.028–3.800 Å, Co···Co···Co 52.8–76.4°, Co–O–Co 91.5(1)–134.6(2)°), compared to that of Δ-(μ_3-O_{10}) (Co···Co 3.189–3.324 Å, Co···Co···Co 58.3–62.5°, Co–O–Co 102.2(2)–114.1(2)°). The two kinds of triangle are corner-shared with a dihedral angle of 141.9° to furnish a geometrical topology akin to a distorted Kagomé lattice (Fig. 1b). Although all the Co^{II} atoms are located at the vertices of a Kagomé lattice, the resulting topological lattice is different from a standard Kagomé lattice not only because the Co^{II} atoms are mixed-geometrical but also because not all the Co^{II} atoms are corner-shared. The tetrahedral Co^{II} atoms are corner- or edge-shared with the octahedral Co^{II} atoms, while the octahedral Co^{II} atoms are only edge-shared with each other (ESI Fig. S1†). The formation of an analogous Kagomé lattice rather than a triangular lattice in **1** with the triangular Co^{II}_3(μ_3-OH) units is greatly related to the length and flexible nature of 1,2-chdc. Each 1,2-chdc is coordinated to five Co^{II} atoms by four oxygen atoms of the two *trans*-related carboxylates, while the hexane ring is almost perpendicular to the cobalt(II) hydroxide layer. These hexane rings act as an organic skin to wrap the layer into a perfect inorganic–organic sandwich structure (Fig. 1c). Such layers are stacked in the *c*-direction only by the van der Waals interactions with the shortest interlayer $Co^{II}\cdots Co^{II}$ distance up to *ca.* 13.6 Å.

The magnetic properties of **1** are shown in Fig. 2.¶ At room temperature, the χT value of **1** is 6.09 $cm^3\ mol^{-1}$ K per Co^{II}_3 unit, which is slightly higher than the spin-only value (5.63 $cm^3\ mol^{-1}$ K) due to the orbital contribution from the single octahedral Co^{II} ions. Upon cooling, it decreases to a minimum at *ca.* 13.6 K and then abruptly increases to reach a maximum at *ca.* 10 K (Fig. 2a). The shape of the χT *vs.* T curve corresponds well to the antiferromagnetism of the Co^{II}_3(μ_3-OH) triangles with an uncompensated ground-state.[1–3] The $1/\chi_m$ *vs.* T plot is very informative. Above 14 K, the plot is exactly a straight line well fitted by the Curie–Weiss law ($\chi_m = C/(T - \theta)$), with C = 7.73 $cm^3\ mol^{-1}$ K, $\theta = -80.33$ K, and $R = 5 \times 10^{-5}$, where $R = \Sigma[(1/\chi_m)_{obs} - (1/\chi_m)_{calcd}]^2/[(1/\chi_m)_{obs}]^2$. The C value corresponds to g = 2.34, which is normal for such a mixed octahedral and tetrahedral Co^{II} system.[8,9] The Weiss constant, which is significantly larger than those of other cobalt(II)-hydroxy compounds,[8–10] indicates a dominated antiferromagnetic coupling between the Co^{II} ions. The value of $f = |\theta/T_N| = 7.3$ (T_N = 11 K defined by ac susceptibility, see below) as well as a wide range of strictly linear $1/\chi_m$ *vs.* T plot above T_N indicate the presence of moderate spin frustration in **1**.[2] The *f* value is smaller than those of iron jarosites ($f > 10$),[1,3] indicating that the distortion of Co^{II}_3(μ_3-OH) triangles weakens the spin frustration.[1–3] Moreover, the χ and χT values are dependent on the applied field at low temperatures (Fig. 2b and ESI Fig. S2†), which is larger at a small field due to the presence of spin canting within the inorganic layers as a result of the tilting of CoO_6 octahedra and CoO_4 tetrahedra, suggesting weak ferromagnetism,[11] which is further confirmed by the facts that the *M*–*H* curves at various temperatures are almost linear (Fig. 2c), reaching the maximum value of 1.26 μ_B, being markedly below the expected 3 μ_B of an antiferromagnetically coupled Co^{II}_3 unit (the value 3 μ_B is estimated by the formula: $M_{sat} = |2 \times g_{oct} \times 3/2 - 1 \times g_{tet} \times 3/2|$, assuming $g_{oct} = g_{tet}$ = 2),[9c] as well as a narrow hysteresis loop observed at 9 K with a small coercive field of 325 Oe and a remnant magnetization of 6.4×10^{-3} μ_B indicating a soft-magnetic behavior of **1** (Fig. 2d). Furthermore, irreversibility of the field-cooled (FC) and zero-field-cooled (ZFC) magnetization below *ca.* 12 K (Fig. 2e) as well as a sharp peak of the ac susceptibility at *ca.* 11 K in both real and imaginary components (ESI Fig. S3†) not only indicate the onset of magnetic LRO, but also exhibit the occurrence of spontaneous magnetization of **1**. In addition, no obvious frequency-dependent behaviour is observed in **1** (Fig. 2f), which precludes the possibility of a spin-glass.[12] Since the inorganic layers are well separated, the occurrence of LRO in **1** is mainly driven by the dipolar interactions between the inorganic layers which have a large effective moment resulting from short-range intralayer interactions.[9]

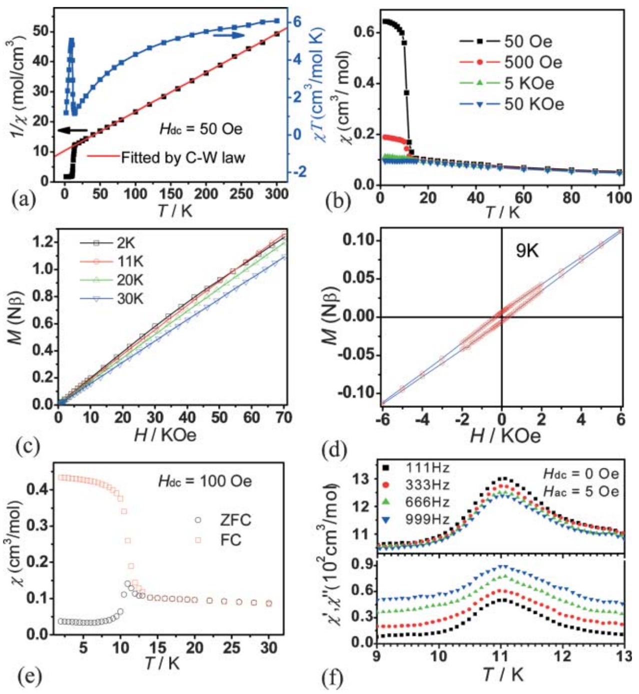
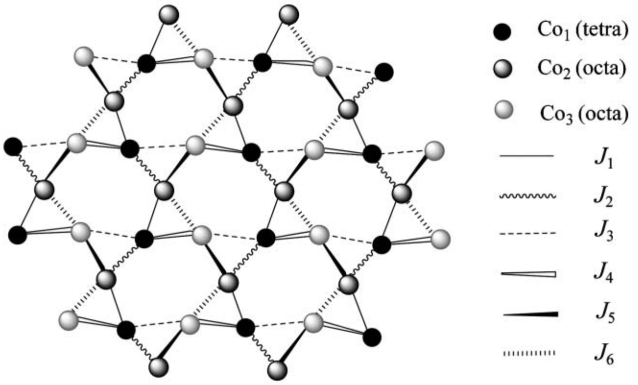


Fig. 2 Plots of χT *vs.* T (blue) and $1/\chi$ *vs.* T (black) (a), χ *vs.* T at various fields (b), isothermal magnetization at various temperatures (c), hysteresis loop (d), field-cooled (FC) and zero-field-cooled (ZFC) magnetization (e) and temperature dependence of ac susceptibility at various frequencies (f) of **1** (lines without specification are eye-guides only).

The magneto-structure of **1** is rather complicated (Scheme 1), and can hardly be quantitatively studied by simple analytical expressions. It should be noted that long range ferro-/antiferromagnetic ordering are commonly found in some layered cobalt compounds.[8b,9] However, these compounds usually do not show



Scheme 1 Illustration of inequivalent-exchange pathways in the Kagomé-like lattice of **1**.

the coexistence of spin frustration. This phenomenon observed for **1** might mainly attributed to two facts: one is the Jahn–Teller distorted Co^{II} sites relieving frustration in one dimension, leading to 2D Ising antiferromagnetism, the other is the formation of the analogous Kagomé lattice with the Co$^{II}{}_3$(μ_3-OH) units since the marginal magnetism of a Kagomé antiferromagnet is a result of competition between LRO and quantum spin fluctuations caused by strong spin frustration (ESI Scheme 3S†).[2,3] In other words, if quantum spin fluctuations are large enough to suppress LRO, a quantum spin liquid may be obtained, and such a ground-state is likely to be found in $S = ½$ Kagomé antiferromagnets,[3] which is partially the case for **1** at low temperatures due to the majority of octahedral Co^{II} ions for the combined action of spin–orbital coupling and noncubic crystal-field terms, giving six Kramers doublets;[4] if the competition is too close to suppress each other, a median state of "order by disorder"[13] is probably established. The coexistence of spin frustration and LRO may be the median state, which is also found in some other compounds possessing a Kagomé lattice such as the Fe^{III}/Cr^{III} jarosites.[6,7] According to some previous studies,[2] LRO in a Kagomé lattice may be established by the presence of further-neighbour exchange interactions, by anisotropy, or by lattice distortion/disorder. All these reasons make the magnetism of a compound with the Kagomé lattice more complex and versatile such as ferromagnetism in the V^{III} jarosites[6] and the dimeric Cu^{II} compound,[14] glassy behavior in the mixed valence Fe^{II}/Fe^{III} compounds[7a] and ferrimagnetism in the Fe^{II} compounds.[7b,d] In contrast, the magnetism of **1** is closer to the Fe^{III}/Cr^{III} jarosites.[6] The analogous, but non-standard Kagomé lattice nature of **1** significantly weakens the frustration between spins, leading to the establishment of LRO.[6]

In summary, **1** represents an unprecedented geometrical topology analogous to a distorted Kagomé lattice based on mixed-geometrical cobalt(II) hydroxide with the aid of carboxylate bridges exhibiting the coexistence of spin frustration and LRO.

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Notes and references

‡ In a typical hydrothermal reaction, a mixture of CoCl$_2$·6H$_2$O (0.474 g, 2 mmol), 1,2-chdcH$_2$ (0.172 g, 1 mmol) and triethylamine (0.300 g, 3 mmol) at a molar ratio 2 : 1 : 1 : 3 in deionised water (10 ml) was sealed in a 23 ml Teflon-lined autoclave and heated at 220 °C for 7 days to give purple plate-like crystals of **1** (yield 88% based on 1,2-chdcH$_2$). The X-ray powder diffraction pattern is shown in ESI Fig. S4.† IR data for **1** ($\bar{\nu}$/cm^{-1}): 3556(w), 3181(w), 2926(s), 2854(m), 1611(s), 1559(vs), 1529(vs), 1422(s), 1321(m), 1329(m), 1277(m), 1115(w), 949(w), 906(w), 868(w), 770(w), 728(w), 689(w), 524(w) cm^{-1}. Anal. Calc. for **1**: C, 34.87; H, 4.02; Found: C, 34.80; H, 4.08%.

§ *Crystal data* for **1**: C$_{16}$H$_{22}$Co$_3$O$_{10}$, M = 551.13, orthorhombic, space group *Pbca*, a = 13.6274(9), b = 10.0360(7), c = 28.558(2) Å, V = 3905.7(5) Å^3, Z = 8, D_c = 1.875 g cm^{-3}, Mo Kα, λ = 0.71073 Å, θ_{max} = 26°, T = 293(2) K, total data 18903, unique data 3838, μ = 2.571 mm^{-1}, 262 parameters, R_1 = 0.0486, wR_2 = 0.1443 on $|F^2|$ and S = 1.073. Bruker SMART Apex CCD diffractometer. The structure was solved by direct methods and all non-H atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using SHELXTL. CCDC 277621. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511612k

¶ Magnetic susceptibility measurements of **1** were performed on a polycrystalline sample (15.3 mg) with random orientation on a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

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