A robust microporous 3D cobalt(II) coordination polymer with new magnetically frustrated 2D lattices: single-crystal transformation and guest modulation of cooperative magnetic properties†‡

Ming-Hua Zeng, a,b Xiaoyong Long Feng, a Wei-Xiong Zhang a and Xiao-Ming Chen* a

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A microporous 3D cobalt(II) coordination polymer featuring pillared layers [Co2(ma)(ina)].2nH2O (1·2H2O) (ma = malate, ina = isonicotinate) was generated by hydrothermal treatment with a void volume of 25.8%, in which the in-situ generated ma ligands connect the Co2+ ions into a 2D lattice with mixed and multiple exchange-bridges, affording a new geometrical topology different from the Kagomé lattice and leading to spin frustration. The rigid ina-pillared metallic-layered structure could retain 3D structural ordering upon guest removal and exchange. By soaking guest-free host (1) in MeOH and methanamide (HCONH2) solutions, single crystals of dehydrated I were transformed into single crystals of 1·MeOH and 1·HCONH2, respectively, without apparent host-structural changes. 1 can also be rehydrated into 1·2H2O. The guest-inclusion crystals have been characterized by X-ray single-crystal diffraction at 293 K and 93 K, confirming the single-crystal-to-single-crystal transformations and providing detailed information of the guest molecules confined in the subnanospace and host–guest and/or guest–guest hydrogen-bonding interactions. The magnetic behaviours of this family of porous magnetic materials are complex due to the influences of multiple metal sites, intra- and inter-layer exchanges, spin–orbit coupling, as well as geometrical frustration, which show magnetic ordering at <2 K, 3.5 K, 3.5 K, and 8 K for 1, 1·MeOH, 1·HCONH2, and 1·2H2O, respectively, due to the different size of guest molecules along with the different host–guest interaction, which may slightly modify the path of magnetic exchange, decrease the intensity of the spin-frustration in the 2D lattice, and cooperatively enhance the magnetic ordering temperature.

Introduction

Magnetic microporous metal–organic frameworks (MOFs) have attracted current interest for multifunctional molecule-based materials.1−4 In contrast to the crucial requirements of short-bridged moment carriers of super-exchange for long-range magnetic ordering, porosity of MOFs usually relies on the use of long connecting ligands, magnetism and porosity are conflicting to each other. Therefore, design of a porous magnet presents a great challenge.1,2,4 The documented porous magnets include metal–organic radical complexes,4 pillared layered metal hydroxides,6 Prussian blue analogs,7 and carboxylate-bridged materials, and so on.8 Some interesting investigations have been reported to deal with modulation of the magnetic properties of porous magnets upon guest exchange or evacuation.5−8 Many of them have been shown to be of obvious host-structure transformations and/or structural collapses, resulting in the obvious changes of the magnetic interaction paths in the magnetic hosts,1,5,8 because of the limited robustness of the host MOFs. Therefore, it is still difficult to make a thorough study of the modulation effect of the guest molecules on the cooperative magnetic properties of such microporous MOFs. The inherent difficulties for the study can be summarized as: (1) the ultimate design is never easy; (2) the final products are often poorly crystallized, hence hampering characterization of their structures and magnetic properties; (3) the overall thermal stability is generally limited to the intrinsic thermal stability of the organic ligand and, therefore, is lower compared with typical inorganic porous materials such as zeolites and (4) since “Nature abhors a vacuum”, many porous MOFs collapse in the absence of the guests.1,2

Robust three-dimensional (3D) microporous MOFs built by pillared layers provide an opportunity for systematic study of the relationship between the guest and magnetic-property through guest exchanges that may perturb the magnetic host. Furthermore, the “inorganic” layers in pillared layered MOFs may be of the so far rarely observed, but theoretically important 2D spin topologies and spin-frustrated lattices, such as the Kagomé or triangle lattice.1,9−11 Meanwhile, with rationally arrayed corner- and edge-shared triangular lattices, a new spin-frustrated 2D topology may be constructed. Such geometrically frustrated antiferromagnetic materials have attracted much attention in recent years due to their propensity to adopt unusual, even exotic magnetic ground states which remain poorly understood.1,9−11
It has been noted that coordination complexes with in-situ generated ligands are of great interest in both coordination chemistry and organic chemistry for discovery of new organic reactions and understanding the reaction mechanisms, as well as for preparation of the coordination architectures that are usually inaccessible via direct use of the ligands. In fact, we were unable to generate “inorganic” laminated compounds using the promising malate (ma) anion as a versatile ligand bearing a hydroxyl group. As fumaric acid can be hydrolyzed into maleic acid, in our continuing effort to generate new magnetic MOF materials using the hydrothermal technique, we chose fumaric acid (and maleic acid or anhydride) as the precursor to prepare a CoII MOF in the presence of isonicotinic acid (Hina) as an additional ligand, giving rise to [Co_{2}(ma)(ina)]_{n}·2nH_{2}O (1·2H_{2}O), in which fumaric acid was converted in situ into racemic ma ligands. These ma ligands connect the CoII ions into 2D spin-frustrated lattices with mixed (ferromagnetic or antiferromagnetic coupling) and multiple exchange-bridges (different coupling intensity) between the magnetic centres, resulting in a frustrated lattice and complicated magnetic properties that can be modulated by guest removal and exchange via single-crystal-to-single-crystal transformations into dehydrated 1, 1-MeOH and 1-HCONH_{2} (Scheme S1).

**Experimental**

**Preparation of 1·2H_{2}O**

Fumaric acid (0.116 g, 1 mmol) (or maleic acid/maleic anhydride) in an aqueous solution (6 mL) of NaOH (0.080 g, 2 mmol) was mixed with isonicotinic acid (0.123 g, 1 mmol) in water (2 mL), which was then added to an aqueous solution (2 mL) of Co(NO_{3})_{2}·6H_{2}O (0.582 g, 2 mmol). The mixture was placed in a 23-mL Teflon-lined autoclave and heated at 170 °C for 140 h. The autoclave was cooled over a period of 12 h at a rate of 5 °C h⁻¹, and 1·2H_{2}O as purple crystals were collected by filtration, washed with water, and dried in air, the final pH of the solution is ca. 6.0. The phasepure 1·2H_{2}O was obtained by manual separation (yield: 102 mg, 25% based on Co). Anal. Calcd. (%) for C_{11}H_{10}Co_{2}N_{2}O_{8}: C, 32.78; H, 2.75; N, 3.47; found C, 32.7; H, 2.82; N, 3.40%. IR data: 3452m, 1614vs, 1583vs, 1554vs, 1403vs, 1311m, 1272m, 1150w, 815w, 772m, 599w.

**Preparation of 1**

Anhydrous 1 was obtained by heating crystals of 1·2H_{2}O in vacuum at 200 °C under a gas pressure blow 4 mmHg for 1 day. The lattice water molecules were completely removed based on the PXRD data and the framework retains structural integrity based on the PXRD data. Although some crystals were cracked, the others retained their primary well-defined external shapes after the heating process.

**Preparation of 1-MeOH and 1-HCONH_{2}**

After immersing reasonable size crystals of 1 in MeOH or HCONH_{2} solvents in small sealed tubes, respectively, at room temperature for one day, the crystals retained their primary well-defined external forms with the microporous space of the crystals accommodating new guest molecules, furnishing crystals of 1-MeOH and 1-HCONH_{2}, respectively, which are stable in the atmosphere. Anal. Calcd. (%) for C_{11}H_{10}Co_{2}N_{2}O_{8}: C, 32.78; H, 2.75; N, 3.47; found C, 32.7; H, 2.82; N, 3.40%. IR data: 3452m, 1614vs, 1583vs, 1554vs, 1403vs, 1311m, 1272m, 1150w, 815w, 772m, 694m, 599w.

**Rehydration of 1**

Standing of 1 in air (T = 22(2) °C, relative humidity = 35(5)%) for six days gave rise to the rehydrated 1·2H_{2}O⁺.

**Magnetic measurements**

Detailed ac and dc magnetic data were collected using a Quantum Design MPMS XL-7-SQUID magnetometer on phase-pure samples from crushed single crystals. The zero-field cooled (ZFC) and field cooled (FC) dc data were recorded in applied fields of 10 Oe in the temperature range of 2–300 K. After heating to 380 K and subsequent cooling down to 300 K, the magnetic data of 1 were collected in the range 2–300 K at 100 Oe. The data for 1-MeOH were recorded on cooling the sample in a helium flow from 275 to 2 K to avoid escape of the guest molecules. The field-cooled magnetization measurements in external fields around the critical metamagnetic field were conducted on cooling from 30 K. The isothermal magnetization data were collected at T < 10 K, in fields of up to 70 kOe. The ac measurements were performed on cooling the samples in a field of 5 or 6 Oe oscillating at 11, 111, 311, 665, 997 Hz.

**Powder X-ray diffraction (PXRD)**

The purities and crystallinities of the bulk samples were checked by PXRD using a Rigaku D/max 2200 diffractometer.
X-Ray crystallography

All diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 or 93 K. Absorption corrections were applied by SADABS. All the structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters except the solvent molecules. The aqua hydrogen atoms were located from the difference Fourier map at the final states of refinement. For all structures, the refinements revealed two-fold disorder of two alkyl (C8, C9) atoms of ma. The disordered guest molecules in 1-MeOH and 1-HCONH₂ were refined in two orientations, and were subjected to geometric restraints during the refinements. On the other hand, the aqua oxygen atoms in 1-2H₂O were refined anisotropically for both the 93 K and room temperature data. All of them were subjected to geometric restraints during the refinements. The water hydrogen atoms in 1-2H₂O were located in the electron density map. The refinement of 1 gave two residual electronic peaks (1.17 and 1.34 e Å⁻³) in the void of I at the final stage of structural refinement, which though smaller than that (1.49 e Å⁻³) around a CoII atom within a distance of 0.90 Å, may imply the presence of trace water molecules during the X-ray measurement as well as lower quality diffraction data. The crystallographic details are provided in Tables 1 and S1‡, while the selected bond distances and angles are listed in Tables S3 and S4‡.

Crystal structures

X-Ray single-crystal diffraction reveals that all the four compounds crystallize in the same space group C2/c with maximum differences in the unit-cell dimensions with volumes being 0.16 Å (0.74%) and 37.0 Å³ (1.3%) at 293 K, and 0.48 Å (2.0%) and 19.3 Å³ (0.70%) at 93 K, respectively (Table 1).

In the as-synthesized 1-2H₂O, the asymmetric unit consists of one ina, one ma and two CoII ions, as well as two lattice water molecules. Co(1) is coordinated by four ma oxygen atoms (Co–O 2.013(3)–2.149(3) Å) and one nitrogen atom and one oxygen atom from ina (2.161(5), 2.089(4) Å) to form a distorted CoO₉N₁ octahedron (OCT), while Co(2) is only ligated by four ma oxygen atoms and one ina oxygen atom (Co-O 1.939(4)–2.114(3) Å) to furnish a distorted CoO₉ (Fig. S1†) trigonal-bipyramid (TBP). Each ma is coordinated to six CoII ions through two 1,3-bridging carboxylate and one ma-alkoxo group, while each ina ligand is ligated to three CoII ions (Scheme 1, Fig. S1‡). This coordination mode therefore results in eight coordination bonds to six CoII ions for each ma, which is the highest coordination number of ma so far documented.¹⁸

The two kinds of CoII ions are alternatively bridged by ma into an infinite undulated [Co₆{(ma)₃}⁺₃]⁺ layer (Fig. 1a,b) with different adjacent Co···Co separations via five exchange-paths (µ-O-bridges: Co₁···Co₂ 3.509(1) Å, Co₁···Co₃ 3.455(1) Å, Co₁···Co₆b 3.312(1) Å, different 1,3-carboxylate-bridges: Co₂···Co₆a 5.392(1) Å, Co₄···Co₆ 5.351(1) Å). This layer is very rigid and can be simply described by alternative connection of the helices of corner sharing OCT and TBP polyhedra by edges-sharing OCT running along the a-axis, which represents the first example of an “inorganic” metal–oxgen layer interconnected uniquely by carboxylate and ma-alkoxo groups without the presence of any hydroxyl groups. Such layers are further pillared by µ-ina ligands into a 3D microporous MOF with the layers stacking in an ABAB mode (Fig. 1c) and the interlayer distance of ca. 9.9 Å.

As no hydrogen-bond donor is present in the host MOF, it can only act as a hydrogen-bond acceptor.¹⁸ The opening size of the saddle-like channels corresponds to 25.8% potential solvent accessible volume (668.6 Å³ per unit-cell volume of 2784.4 Å³),¹⁹ where the guest water molecules are anchored to the layers by guest-host hydrogen bonds [O₁W···O2' 2.78(2), O₂W···O4 2.97(2) Å, Table 3]. These guest molecules are also interlinked by hydrogen bonds [O₂W···O₂W' 3.18(3), O₁W···O₂W' 2.70(2) Å]

Table 1 Crystallographic data and structure refinements

<table>
<thead>
<tr>
<th>Compound</th>
<th>1-2H₂O</th>
<th>1-2H₂O</th>
<th>1-MeOH</th>
<th>1-MeOH</th>
<th>1-HCONH₂</th>
<th>1-HCONH₂</th>
<th>1</th>
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<tbody>
<tr>
<td>T/K</td>
<td>293</td>
<td></td>
<td>93</td>
<td></td>
<td>293</td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>Formula</td>
<td>C₃H₃Co₂NO₃</td>
<td>C₃H₃Co₂NO₃</td>
<td>C₃H₃Co₂NO₃</td>
<td>C₃H₃Co₂NO₃</td>
<td>C₃H₃Co₂NO₃</td>
<td>C₃H₃Co₂NO₃</td>
<td>C₃H₃Co₂NO₃</td>
</tr>
<tr>
<td>FW</td>
<td>407.06</td>
<td>407.06</td>
<td>403.07</td>
<td>403.07</td>
<td>416.07</td>
<td>416.08</td>
<td>371.03</td>
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<tr>
<td>a/Å</td>
<td>23.550(2)</td>
<td>23.226(2)</td>
<td>23.457(3)</td>
<td>23.521(2)</td>
<td>23.583(3)</td>
<td>23.702(3)</td>
<td>23.402(3)</td>
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<tr>
<td>b/Å</td>
<td>10.082(1)</td>
<td>10.107(1)</td>
<td>10.094(1)</td>
<td>10.268(1)</td>
<td>10.104(1)</td>
<td>10.062(1)</td>
<td>10.061(1)</td>
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<tr>
<td>c/Å</td>
<td>14.978(2)</td>
<td>14.890(1)</td>
<td>15.044(2)</td>
<td>14.985(1)</td>
<td>15.060(2)</td>
<td>15.020(2)</td>
<td>14.950(2)</td>
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<td>β/°</td>
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<td>127.81(1)</td>
<td>128.249(2)</td>
<td>128.618(1)</td>
<td>128.540(2)</td>
<td>129.07(2)</td>
<td>128.342(2)</td>
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<td>V/Å³</td>
<td>2784.4(5)</td>
<td>2761.6(3)</td>
<td>2797.3(7)</td>
<td>2761.5(3)</td>
<td>2806.8(6)</td>
<td>2780.9(5)</td>
<td>2769.8(6)</td>
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<td>D, g cm⁻³</td>
<td>1.942</td>
<td>1.958</td>
<td>1.914</td>
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<td>1.969</td>
<td>1.988</td>
<td>1.780</td>
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<td>2.449</td>
<td>2.412</td>
<td>2.443</td>
<td>2.424</td>
<td>2.411</td>
<td>2.422</td>
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<td>R₂(rms)</td>
<td>0.0357</td>
<td>0.0324</td>
<td>0.0600</td>
<td>0.0398</td>
<td>0.0389</td>
<td>0.0360</td>
<td>0.0278</td>
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<td>R₁ (f &gt; 2σ)</td>
<td>0.0457</td>
<td>0.0538</td>
<td>0.0505</td>
<td>0.0583</td>
<td>0.0569</td>
<td>0.0490</td>
<td>0.0471</td>
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<tr>
<td>wR₂(rms)</td>
<td>0.1124</td>
<td>0.1229</td>
<td>0.1398</td>
<td>0.1458</td>
<td>0.1644</td>
<td>0.1237</td>
<td>0.1295</td>
</tr>
<tr>
<td>GOE</td>
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<td>1.08</td>
<td>1.000</td>
<td>1.22</td>
<td>1.06</td>
<td>1.13</td>
<td>1.02</td>
</tr>
<tr>
<td>ΔV/conf</td>
<td>-0.57±0.83</td>
<td>-0.72±1.16</td>
<td>-0.86±0.66</td>
<td>-0.98±2.31</td>
<td>-1.09±1.37</td>
<td>-0.69±1.40</td>
<td>-0.55±1.49</td>
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<tr>
<td>Free volume</td>
<td>25.8%</td>
<td>24.9%</td>
<td>25.1%</td>
<td>25.1%</td>
<td>26.6%</td>
<td>25.6%</td>
<td>24.1%</td>
</tr>
</tbody>
</table>

R₁ = Σ||Fᵣ| - |F₀||²/Σ(F₀)², wR₂ = [Σw(F₁ - F₀)²/Σ(F₀)²]¹/².
Meanwhile another trio is formed by two of edge-sharing bridges (Co$_2$) may favor ferromagnetic interactions, and ultimately leading to spin glass behaviour at low temperature.

<table>
<thead>
<tr>
<th>Exchange Bridges</th>
<th>1·2H$_2$O (293 K)</th>
<th>1·2H$_2$O (93 K)</th>
<th>1·MeOH (293 K)</th>
<th>1·MeOH (93 K)</th>
<th>1·HCONH$_2$ (293 K)</th>
<th>1·HCONH$_2$ (93 K)</th>
<th>I (293 K)</th>
<th>Max deviation at 93 K</th>
<th>Max deviation for all temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1···O3···Co2</td>
<td>113.5(1)</td>
<td>113.5(1)</td>
<td>114.2(2)</td>
<td>113.7(1)</td>
<td>113.9(1)</td>
<td>113.9(1)</td>
<td>114.2(1)</td>
<td>113.6(1)</td>
<td>0.62%</td>
</tr>
<tr>
<td>Co1···Co2</td>
<td>3.509(1)</td>
<td>3.503(1)</td>
<td>3.522(1)</td>
<td>3.510(1)</td>
<td>3.521(1)</td>
<td>3.517(1)</td>
<td>3.503(1)</td>
<td>0.43%</td>
<td>0.54%</td>
</tr>
<tr>
<td>Co1···O6···Co1$^+$</td>
<td>101.6(1)</td>
<td>101.6(1)</td>
<td>101.5(1)</td>
<td>100.6(1)</td>
<td>101.8(2)</td>
<td>101.1(1)</td>
<td>101.7(1)</td>
<td>0.98%</td>
<td>1.29%</td>
</tr>
<tr>
<td>Co1···Co1$^+$</td>
<td>3.312(1)</td>
<td>3.299(1)</td>
<td>3.318(1)</td>
<td>3.283(1)</td>
<td>3.323(1)</td>
<td>3.300(1)</td>
<td>3.305(1)</td>
<td>0.52%</td>
<td>1.22%</td>
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<tr>
<td>Co1···O5···Co2$^+$</td>
<td>121.9(1)</td>
<td>121.1(1)</td>
<td>122.4(2)</td>
<td>121.8(1)</td>
<td>122.4(2)</td>
<td>122.2(1)</td>
<td>121.8(1)</td>
<td>0.25%</td>
<td>0.41%</td>
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<tr>
<td>Co1···Co2$^+$</td>
<td>3.455(1)</td>
<td>3.452(1)</td>
<td>3.466(1)</td>
<td>3.455(1)</td>
<td>3.475(1)</td>
<td>3.467(1)</td>
<td>3.449(1)</td>
<td>0.43%</td>
<td>0.52%</td>
</tr>
<tr>
<td>Co1···O···Co···Co2</td>
<td>5.351(1)</td>
<td>5.299(1)</td>
<td>5.367(1)</td>
<td>5.338(1)</td>
<td>5.407(1)</td>
<td>5.391(1)</td>
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<td>0.78%</td>
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<tr>
<td>Co2···O···Co···Co2$^+$</td>
<td>5.392(1)</td>
<td>5.402(1)</td>
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<td>5.365(1)</td>
<td>5.407(1)</td>
<td>5.391(1)</td>
<td>5.381(1)</td>
<td>0.69%</td>
<td>0.78%</td>
</tr>
<tr>
<td>Co1···ma···Co$^+$</td>
<td>9.238(1)</td>
<td>9.200(1)</td>
<td>9.231(1)</td>
<td>9.207(1)</td>
<td>9.240(1)</td>
<td>9.217(1)</td>
<td>9.227(1)</td>
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<td>0.43%</td>
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<tr>
<td>Co2···ma···Co$^+$</td>
<td>8.940(1)</td>
<td>8.946(1)</td>
<td>8.940(1)</td>
<td>8.923(1)</td>
<td>8.959(2)</td>
<td>8.952(1)</td>
<td>8.929(1)</td>
<td>0.33%</td>
<td>0.40%</td>
</tr>
</tbody>
</table>

Symmetry codes: $a$ 0.5 $- x$, 1 $- y$, 0.5 $- z$; $b$ 0.5 $- x$, 1.5 $- y$, $- z$; $c$ 2 $- y$, $z$ $- 0.5$; $d$ 0.5 $- x$, 0.5 $+ y$, 0.5 $- z$; $e$ 0.5 $+ x$, 1.5 $- y$, 0.5 $+ z$.

(Fig. S2). Each water molecule occupies a pore volume of 41.8 Å$^3$ (cf. packing density of 19 Å$^3$ per H$_2$O in ice) in 1·2H$_2$O, indicating that they are loosely packed in the 1D channels. It is interesting to note that all the carboxylate oxygen atoms associated with hydrogen bonds come uniquely from the TBP polyhedra, and that the interlayer regions are achiral because the fumaric acid has been converted into the racemic ma ligand during the hydrothermal procedure.

Lattices with the spin carriers lying at the vertices of triangles provide examples of spin-frustrated materials in the presence of antiferromagnetic coupling. According to Goodenough rules, μ-O-bridged Co1···Co2, Co1···Co2$^+$ and Co1···Co1$^+$ interactions are predicted to be antiferromagnetic since the superexchange Co–O–Co angles are only 101.6(1) $-$ 122.0(1)$^\circ$ (Table 2). The anti–anti or syn–syn carboxylate bridges may also favor antiferromagnetic coupling, while the syn–anti carboxylate bridges (Co2···Co2$^+$ and Co1···Co2) may favor ferromagnetic coupling. Two types of triangular frustrated “plaquettes” are created in 1·2H$_2$O (Scheme 2a). Among them, one type of three-membered ring trio is formed by one OCT (via the μ-O-bridges) and two vertex-sharing TBP (through syn–anti 1,3-carboxylate bridges) polyhedra, furnishing an isosceles triangle (IT$_1$, pale blue). Meanwhile another trio is formed by two of edge-sharing OCT and one of corner-sharing TBP polyhedra (through one or three-atom bridges, respectively), giving rise to a distorted isosceles triangular lattice (IT$_2$, green). The IT$_1$ triangles with vertex-sharing TBP polyhedra form a Δ-chain structure (Scheme 2b), which has been the subject of extensive theoretical investigations, yet very few real examples are known. Adjacent antiparallel Δ-chains are linked each other with edge-shared OCT pairs, furnishing a distorted infinite 2D lattice (Scheme 2b). The 2D lattice is best described as a new incomplete occupation of the triangle net different from the Kagomé-triangle lattice (Scheme 2c,d), in which the adjacent Δ-chains are interlinked by sharing the same vertices. It is worthy of note that the vertices of the adjacent Δ-chains in the lattice of 1·2H$_2$O are not shared, which is another topology of possible topological spin frustration. To our knowledge, no incomplete-triangle lattice of the type found in 1·2H$_2$O has been reported. Here, the topological frustration should be expected to cause a large degeneracy in the ground state manifold, and long-range magnetic ordering may be suppressed or significantly reduced as a result of competing antiferromagnetic interactions. Frustration may also be a consequence of disorder, which produces a random combination of ferro- and anti-ferromagnetic interactions, and ultimately leading to spin glass behaviour at low temperature.
Thermal stability of the MOF in 1·2H₂O

The TGA curve of 1·2H₂O shows that the first weight loss of 8.2% between 25 and 260 °C corresponds to the loss of the lattice water molecules (ca. 8.8 wt%), and that the MOF could retain structural integrity to ca. 280 °C and 340 °C in flowing air and dinitrogen, respectively (Fig. S3†). Such striking thermal stability can be ascribed to the strong intra- and inter-layer connections. It was also observed that anhydrous 1 was found to be active, taking up water molecules to form 1·2H₂O. The rehydration rate depends on the time in the open air, the 20–200 °C TGA measurement (Fig. S4†) in air revealed that 1 reabsorbed atmospheric water to 1·0.75H₂O after one day, to 1·1.5H₂O after three days, and to recovery (1·2H₂O) after six days.

Crystal transformations via dehydation, rehydration and guest exchange

Upon appropriate heating, the crystals of 1·2H₂O yielded crystals of anhydrous 1. Subsequent crystal structural analysis indicates minor differences in the unit-cell parameters compared to its parent crystal, as shown in Table 1. This observation can be attributed to the rigid MOF structure in 1·2H₂O, compared to other pillared-layer systems with conformationally flexible pillars that exhibited marked host-structure transformations upon dehydration. In fact, 1 possesses a smaller unit-cell volume only by 0.52% than that of its parent 1·2H₂O with the detailed geometric data (Co–N 2.161(4) Å; Co–O 1.939(4)–2.143(3) Å) resembling those of 1·2H₂O within minor deviations (Tables S3 and S4†). The intradimer Co1···Co2 distance in the asymmetric unit is 3.503(1) Å, and the Co···Co distances bridged by ina ligands are 9.227(1) and 8.929(1) Å in 1, which possesses voids of 24.1% volume of the unit cell. Meanwhile, the geometric data of the rehydrated 1·2H₂O are highly similar to those of 1·2H₂O, although the crystal structure of 1·2H₂O was refined to give a larger R₁ factor than the parent crystal (R₁ 6.34% vs. 4.57%, Tables 1 and S1†).

Because of the high MOF stability of 1·2H₂O, we were able to employ a two-step approach for complete exchanges of the water molecules into other organic guests, i.e. through dehydation of single crystals of 1·2H₂O into anhydrous single crystals of 1. Immersing the fresh anhydrous single crystals of 1 into polar organic solvents MeOH and HCONH₂ at room temperature in small sealed tubes for one day generated new crystals of 1·MeOH and 1·HCONH₂, in which some were of good quality for single-crystal X-ray diffraction.

Both 1·MeOH and 1·HCONH₂ are isomorphous to 1·2H₂O and the host-framework are retained to host the organic solvent molecules, as shown in Table 1 and Scheme S1†. Since MeOH molecule is larger than a water molecule, two H₂O molecules are replaced by one MeOH molecule, and the unit-cell volume of 1·MeOH increases very slightly by 0.46%, whereas the free volume of MOF in 1·MeOH (25.1%) is slightly contracted, compared to that of 1·2H₂O (25.8%). On the other hand, in the presence of HCONH₂ molecules, the structure of 1·HCONH₂ is expanded by 0.80% cell volume and the MOF has a free volume of 26.6%, due to the larger guest molecules (Tables 1 and S1†).

Hydrogen bonding interactions

The robust host MOFs provide a unique opportunity for systematically exploring the relationship between the guest and...
magnetic-properties or the modulation triggered by guest molecules in cooperative magnetic properties since weak interaction perturbation of the magnetic host may be achieved through the exchange of guest species and understood with the aid of the detailed hydrogen bond interactions in crystal structures. According to the criteria of Steiner and Saenger (C···H···O < 2.8 Å and D···H···A > 90°, where D and A are hydrogen donor and acceptor, respectively), the C···H···O hydrogen bonds between pillar-to-host and guest-to-pillar could be neglected in our case, while both guest–host, guest–guest hydrogen-bonding interactions may be present (see Table 3, Scheme 3 and Fig. S2, S5 and S6†). As shown in Scheme 3, four water molecules in channels are located close to each other and all hydrogen bonds with the O4 or O7 atoms ligated to the TBP CoII ions are of the same kind. The guest–host and guest–guest hydrogen–guest hydrogen bond interactions (O···O 2.70(2)–3.18(3) Å at 293 K and 2.63(1)–2.93(1) Å at 93 K) link the adjacent layers together (Fig. S3) with double O···O···O···O hydrogen bond bridges. It should be noted that only one negligible hydrogen bond (O2W···O2Wg 3.18(3) Å) between two adjacent water dimers is found in the 293 K structure, while there are hydrogen bonds (O2W···O1W′ 2.93(2) Å) in the 93 K case.

The HCONH2 and MeOH molecules have poorer hydrogen donor abilities than H2O. Each HCONH2 or MeOH molecule donate only one weak hydrogen bond to the O4 or O7 atoms ligating the TBP CoII ions, respectively, being similar to the water molecules. The MeOH molecule forms the guest–host hydrogen bonds (O8···O4 2.96(3) or O8···O7 2.84(3) Å at 293 K, O8···O4 2.95(1) Å at 93 K) and thus anchors onto the layer. The HCONH2 molecule exhibits similar guest–host hydrogen bonds.

The different locations of guest molecules and guest-host/guest–guest hydrogen-bonding interactions are also related to the temperature and guest. In particular, the guest water molecules tend to form more intensive supramolecular interactions at low temperature. The weaker donor abilities, concomitant with larger sizes, of the organic molecules only exhibit weaker host–guest hydrogen bonds without the presence of guest–guest hydrogen bonds. More importantly, the conditions for magnetic frustration are satisfied in I and the different hydrogen-bonding interactions to the geometrical frustrated layers in the different cases may be expected to influence the frustration within and between the layers at low temperature (see below), which has not been described.

**Discussion on crystal transformations**

Single-crystal structurally characterized desolvated forms of relevant MOFs are so far rare, thus this work provides an unusual example of stable magnetic microporous MOF structurally characterized by single-crystal X-ray diffraction in both solvated and desolvated forms. The perfect crystallinities in the transformed products should be attributed to the fact that the thicker layers pillared by rigid ina ligands are very stable and the guest molecules (including H2O, CH3OH and HCONH2) do not play any significant role in consolidating the MOFs. The crystal-to-crystal transformations only involve slightly structural expansions from 1H2O to 1-HCONH2 and from anhydrous I to 1H2O, as well as a slight contraction from 1H2O to I (±1.6% in cell volume). The largest deviations of the bond lengths and bond angles are 0.91% and 2.85% for the eight structural data measured at 293 and 93 K, respectively (Tables S3 and S4†), which also suggest marked robustness of the host MOFs. In the 93 K data of guest-inclusions, the deviations in the lengths of dominating exchange bridges between the adjacent CoII ions within the layer are less than 1.2%, and those in the bond angles are less than 1% (Table 2). In particular, the deviations of the lengths associated with ina are only ca. 0.33%, which is a less obvious change for magnetic interactions. Therefore, our observations support the suggestion of using single-crystal transformation as a crystal engineering strategy on a subnanometric scale for making fine adjustments of magnetic properties by systematically varying the identity and ratio of guests.

**Magnetic studies**

The magnetic data were measured by tightly putting the crushed polycrystalline samples together to prevent torquing of the crystallites. The magnetic susceptibility curves for 1H2O, 1-HCONH2, 1-MeOH and I show the expected behaviour for a simple paramagnet at 300 K down to ca. 20 K (Fig. S7†) obeying the Curie–Weiss law at high-temperature with Landé g-values of 2.00, C = 5.82 to 6.61 cm³ mol⁻¹ K, \(\theta = -45.2\) to \(-60.2\) K, and \(\mu_{eff} = 6.25\) to 6.67 mpb per CoII (Table 4), indicative of significant antiferromagnetic coupling and/or spin–orbital coupling between the CoII ions. Below 20 K deviations from Curie–Weiss behaviour due to the onset of single-ion anisotropy and short-range ordering were observed for 1H2O, 1-HCONH2 and 1-MeOH.

**Complex 1H2O.** The \(\mu_{eff}\) for 1H2O decreases gradually to ca. 50 K before falling off rapidly down to 15 K, while it decreases sharply at lower temperatures and exhibits a shoulder at around 12 K likely attributed to a spin-canted behaviour;
which is confirmed by the divergence between the zero-field-cooled (ZFC) and field-cooled (FC) which is characteristic of both spin-glass and spin-canted behaviours (Fig. 2). The ac magnetic susceptibility measurements for 1·2H₂O show slight frequency shift peaks of $\chi'$ and $\chi''$ at 8 K ($T_N$), indicating a phase transition to antiferromagnetic ordering and weak spin glass behaviour below the temperature 8 K.²⁵,²⁶

The 2 K isotherm clearly indicates that even with 70 kOe the saturation is not reached ($M = 1.70 N\beta$) (Fig. S8‡). The occurrence of an obvious hysteresis loop is observed clearly at 2 K when the field is less than 2000 Oe, giving a coercive field of ca. 93 Oe and a small remnant magnetization of ca. 27 emu Oe mol⁻¹. This fact suggests the presence of weak ferromagnetic interactions, and is indeed a feature of 2D spin-frustrated lattices in 1·2H₂O (Fig. S9‡). The degree of frustration can be quantified by $f = |\theta| / T_N = 6.1$ to be moderate and consistent with a partial frustration to have a suppressed critical temperature, attributable to the distorted geometrical frustrated lattice of 1·2H₂O.⁶–¹¹ which results in disruption of a perfect antiferromagnetic ordering by introducing spin frustration, multiple metal sites and mixed exchange bridges, as well as the single-ion magnetic anisotropy exchange mechanism, leading to the appearance of effective weak ferromagnetic order.¹¹

The temperature dependence of the magnetization of 1·2H₂O at various fields (Fig. 3) illustrates that the more applied fields is associated with the lower value of $\chi$ without a maximum, indicating no field-induced transition.¹⁴

**Complex 1·MeOH.** The value $\mu_{\text{eff}}(T)$ decreases similarly to that of 1·2H₂O and exhibits a shoulder around 4 K. The ac magnetic measurements for 1·MeOH show the small peak at 3.6 K ($\chi'$), indicating a phase transition to magnetic ordering $T_N$; no obvious peak of the out-of-phase signal ($\chi''$) was found, being different from 1·2H₂O.²⁷ Meanwhile, the ZFC/FC data also display a sharp kink at 3.5 K due to the aforementioned canting (Fig. 2). The degree of frustration $f$ of 12.9 for 1·MeOH is strong and consistent with a more partial frustration to have a more suppressed critical temperature, along with a lower value of moment ($M = 1.40 N\beta$) at 70 kOe in the 2 K isotherm (Fig. S10‡). The temperature dependence of the magnetization of 1·MeOH at various fields is shown in Fig. 3. For applied fields below 500 Oe, the FC curves present a maximum at 3.5 K, indicating that some interlayer antiferromagnetic interactions are operative. However, a magnetic field above 750 Oe is sufficient to overcome these weak interactions and 1·MeOH presents a field-induced transition from an antiferromagnetic to a ferromagnetic-like state.⁴⁺,²⁹,³⁰

The magnetization curves (Fig. S10‡) for different temperatures below transition (2 and 3 K) exhibit a sigmoidal shape without an obviously common crossing point. Below the transition, the isotherms have the characteristic of a metamagnet, which is commonly observed in layered compounds⁹ due to the strong structural anisotropy and competitions between the exchange interactions.

**Complex 1·HCONH₂.** The magnetic behaviour of 1·HCONH₂ resembles largely that of 1·MeOH, showing a phase transition to magnetic ordering $T_N$ (3.6 K) without an obvious peak of out-of-phase signal ($\chi''$) indicating a less canted ground state,²⁷ and displaying a sharp kink at 3.5 K due to the above-mentioned canting. The magnetization curves below transition (2 and 3 K) exhibit a sigmoidal shape and a magnetic

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**Table 4** Summary of the magnetic properties for the four compounds

| Complex       | $\mu_{\text{eff}}(\text{ZFC})$ | $C$ | $\theta$ | $T^*$/K (ac 111 Hz) | $M$ (N/µmol at 70 kOe, 2 K) | $T_N$ (at FC–ZFC) | $f = |\theta| / T_N$ |
|---------------|-------------------------------|-----|----------|------------------|---------------------------|------------------|----------------------|
| 1·2H₂O        | 6.67                          | 6.32 | 6.25     | 6.44             |                           |                  |                      |
| 1·MeOH        | 6.61                          | 5.94 | 5.82     | 6.24             |                           |                  |                      |
| 1·HCONH₂      | 48.6                          | 12.9 | 16.6     | 6.1              |                           |                  | >30                  |

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Fig. 2  The FCM and ZFCM measured under an applied field of 10 G for 1·2H₂O, 1·HCONH₂, 1·MeOH, and 1. Inset: The temperature dependence of the in-phase ($\chi'$), and out-of-phase ($\chi''$) ac magnetic susceptibilities.
against a spin-glass interpretation.

The magnetic behaviours of the four compounds arise from the dominant intralayer antiferromagnetic interactions between two sublattices (OCT and TBP) producing a decrease in the moment (up to 70 kOe). In particular, the degree of frustration (f) increases in the order of 1·HCONH₂, 1·MeOH, 1·HCONH₂, and 1, suggesting that different guests, along with different guest–host hydrogen-bonding interactions result in small changes in magnetic exchange of the host-framework, the geometrical frustration behaviour and spin-canting. Such hydrogen bonding interactions are associated with coordinated ma oxygen atoms around the CoIII centres in the host framework and may perturb the geometries and electronic environments of the spin centres. The interlayer antiferromagnetic coupling mediated by the long, covalent aryl ina-bridges is expected to be weak but required for 3D ordering. On the other hand purely electrostatic dipolar interactions between the layers can be less effective at a large distance since the effective moments are due to the spin-frustrated intralayer interactions. Therefore, it may be concluded that the perturbation through the slight structure modifications and host–guest and guest–guest weak interactions, such as hydrogen-bonding interactions, have a discernible effect on spin-frustration behaviour, which result in a cooperative influence upon the transition temperature. The higher transition temperature is related to the increased number and strength of guest–host interactions, such as hydrogen bonding interactions to the 2D lattices of 1·H2O, 1·MeOH and 1·HCONH₂, compared to that of 1. The cooperative paramagnet behaviour of susceptibility down to 2 K for 1 implies a higher degree of geometric frustration due to the absence of hydrogen bonding to the layers.

A strikingly different feature for 1·H2O compared to 1·MeOH and 1·HCONH₂ is the slight spin-glass behaviour. In the vast

Discussion on magnetic behaviours

The magnetic behaviours of the four compounds arise from the dominant intralayer antiferromagnetic interactions between two sublattices (OCT and TBP) producing a decrease in the temperature dependence of the moment. As the two dominating Co···Co superexchange interactions through the –Co–O–Co–O–Co-pathway in the A direction are shorter than those in the B direction (Scheme 2a), the antiferromagnetic interaction alone the A direction is expected to be stronger than that of the B direction along the other three edges of the triangle. It is well known that only interchain interactions can lead to ordering with spontaneous magnetization, and in a 2D system long-range ordering occurs only in the Ising limit. The total effect of interlayer magnetic interaction led to the magnetic ordering of 1·H2O, 1·HCONH₂, 1·MeOH where only 1·H2O shows very clear evidence for long range magnetic order while the other three plots of 1·HCONH₂, 1·MeOH and 1 do not show such a clear bifurcation of FC and ZFC plots nor do the ac insets show maxima in χ′. Due to the distortion of the triangular array top not being equilateral, spin frustration remains plausible, with fewer ground state degeneracies and spin canting. The magnetically ordered state displays irreversibility between FC and ZFC magnetization. In zero field, the presence of both OCT and TBP centres may produce more than two antiferromagnetic sublattices, and the associated canting will produce domain effects giving rise to the FC/ZFC hysteresis. As revealed by the X-ray structures at 93 K, the deviations of magnetic interaction paths of the dominating exchange between intralayer neighbouring CoIII ions are minor for Co–O–Co and Co–O–C–O–Co bridges (Fig. 2 and Table 2). Such small changes may have a proper influence in the change of intralayer magnetic exchange, as well as the dominant antiferromagnetic interaction and spin frustration during the single-crystal structure transformations. On the other hand, as shown in Tables 3 and 4 and Scheme 3, the more and stronger guest–host hydrogen bonding interactions with the layers, the more obvious hysteresis behaviour and larger moment (up to 70 kOe/2 K). In particular, the degree of frustration (f) from 6.3 to >30 increases in the order of 1·H2O, 1·MeOH, 1·HCONH₂, and 1, suggesting that different guests, along with different guest–host hydrogen-bonding interactions result in small changes in magnetic exchange of the host-framework, the geometrical frustration behaviour and spin-canting. Such hydrogen bonding interactions are associated with coordinated ma oxygen atoms around the CoIII centres in the host framework and may perturb the geometries and electronic environments of the spin centres.

Complex 1. In contrast, in the lack of a sharp increase of χ, the μeff of 1 decreases down to the lowest attainable temperature of 2 K, reaching a minimum effective moment value of 1.586 μB without a shoulder and no divergence between the ZFC and FC, and no frequency peaks were found for 1. χ(T) gives a behaviour analogous to that of χ(T) and shows no evidence of frequency dependence and peaks. Obviously, even down to 2 K, no sharp transition indicative of magnetic order was observed, suggesting TN < 2 K. The 2 K isotherm indicates the smallest moment (M = 1.19 μB) at 70 kOe. In contrast to the guest-inclusions, no frequency peaks were found for 1. The field-dependent magnetization does not display a hysteresis loop in this system, indicating a more traditional paramagnetic behaviour.9,11a

Fig. 3 Magnetization (χ) versus T at different applied fields for 1·H2O, 1·HCONH₂ and 1·MeOH.
majority of spin glasses, the microscopic conditions of site disorder and frustration are concomitant.\textsuperscript{15,16}\ The above observation suggests that spin frustration is important to the spin-glass behaviour of 1\textsuperscript{2}H\textsubscript{2}O. Note that the frustration creates a multidegenerate, metastable, frozen ground state for the spin glass, and it is a necessary, but not a sufficient condition for a spin glass.

The magneto-structural correlation indicates that there exists a strong structural anisotropy in 1, which may lead to metamagnetic-like behaviours, such as in the cases of 1\textsuperscript{H}CONH\textsubscript{2} and 1-MeOH.\textsuperscript{12,13}\ The reason why 1\textsuperscript{2}H\textsubscript{2}O does not have a metamagnetic-like behaviours is not yet clear. Presumably, the different contributions of the guest-host hydrogen bonding, magnetic anisotropy, as well as the alignment of the moment to 2D lattice in the crystal lattices, may play a cooperative role for this phenomenon.\textsuperscript{12,14}\ From a magnetic point of view, these compounds are of additional interest for three reasons. Firstly, the new triangular arrangement of the spin carriers is of theoretical importance with regard to frustration\textsuperscript{14,15}\ and to the question of long-range order in two dimensions.\textsuperscript{16}\ Secondly, the guest molecules can tune magnetic exchanges without drastic host-framework change, and such a strategy may also allow introduction of other spin carriers, optically active molecules and electron or hole carriers for creating structures with combined properties.\textsuperscript{12}\ Thirdly, when the layers are well separated, they can be considered as multiple stacks of single layer magnets.\textsuperscript{16,17}\ 

Conclusions

This work demonstrates a rare example of single-crystal-to-single-crystal transformations of the highly stable, pillared layered microporous 3D MOF 1\textsuperscript{2}H\textsubscript{2}O triggered by dehydration, rehydration, and two-step guest exchange into 1-MeOH or 1-HCONH\textsubscript{2} by X-ray single-crystal diffraction, which underscores the potential afforded by rational molecular assembly with in-situ generated ligands for the design of microporous molecular magnets. The stable, microporous magnetic MOF not only exhibits a new 2D geometrical frustration topology different from the Kagomé lattice and complex magnetism due to the influences of multiple metal sites, intra- and inter-layer exchanges, spin–orbit coupling, and geometrical frustration, but also allows the formation of different guest–host hydrogen-bonding interactions via alterations of the guest molecules. The results illustrate that such slight structural modifications via crystal-transformation, along with the guest–host interactions, can tune the geometrical frustration behaviour and the intra-layer antiferromagnetic ordering, leading to unprecedented, dramatic changes of magnetic properties. Therefore, this work represents a systematic study of the modulation in spin-frustrated microporous magnetic system upon alterations of guest molecules within a robust host-lattice.\textsuperscript{7,11,18}\ and supports the optimistic forecast that crystal engineering may allow systematic design of magnetic microporous MOFs.\textsuperscript{1–8}\ 

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