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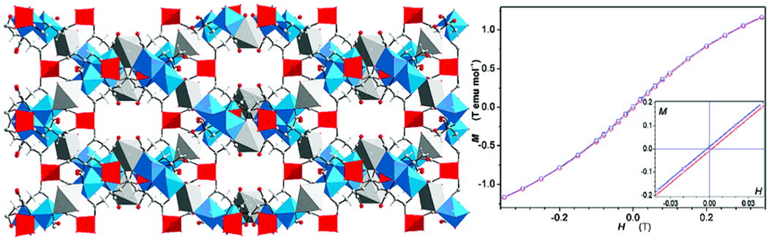

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A 3D Canted Antiferromagnetic Porous Metal−Organic Framework with Anatase Topology through Assembly of an Analogue of Polyoxometalate

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The current interest in crystal engineering of porous metal−organic frameworks (MOFs) stems not only from their potential applications[1] but also from their intriguing variety of architectures and topologies.[2] A new trend in this field is to add functionalities other than porosity to these materials to achieve multifunctional materials.[3] The creation of a porous magnet is a long-sought academic goal since magnetism and porosity are hostile to one another.[4] While long-range magnetic ordering needs spin carriers of short separation through short bridges, porosity relies on the use of extended connecting ligands. Past studies have shown three solutions to this antagonism: to use rigid open-shell organic radicals as polytopic ligands;[5] to connect the polymetal units, such as Cu_2,[6] V_3,[7] and Fe_3,[8] through rigid linkers; or to link infinite M−O−M connectivies through flexible aliphatic dicarboxylate ligands.[9] However, no attempt has been made to use organo-polymetal clusters as bridging units to link metal ions, similar to the behavior of polyoxometalates[10] or cyanoligated species[11] in the assembly of magnetic porous solids, which possibly exhibit desirable pores and improved magnetic properties through cluster-to-metal coupling.[11] To realize this target, we selected citric acid, a more flexible ligand, because it has been widely used to produce high-nuclearity magnetic clusters.[12,13] A more important reason is that the presence of lots of O atoms at the periphery of the clusters can make them versatile building blocks as polyoxometalates to construct novel magnetic porous frameworks with interesting structure topology and physical properties.

Herein, a novel 3D canted antiferromagnetic porous MOF, $\{[KCo_3(C_6H_4O_7)(C_6H_5O_7)(H_2O)_2]\cdot 8H_2O\}_n$ (**1**), is reported with a magnetic hysteresis loop observed at 2 K. To date, only a few compounds with a truly porous framework are known to exhibit long-range magnetic order,[3b,5,6a,9,11] and of those only one inorganic compound has been shown to display magnetic hysteresis.[11]

Hydrothermal reaction of a suspension of cobalt acetate, citric acid, and KOH in ethanol−aqueous solution at 120 °C gave violet prismatic crystals of **1**.[14] Single-crystal X-ray analysis of **1** reveals a 3D open-framework structure constructed from tetrahedral Co^{II} atoms as trigonal nodes and tetranuclear cobalt citrate clusters as octahedral linkers. The structure of the Co_4 cluster here is similar to that of the Co_4 core in a Co_6 single-molecular magnet (SMM).[12a] Through carboxylate groups in an *anti*−*syn* bridging mode, four symmetry-related citrate ligands encapsulating the Co_4 core are further bonded to six tetrahedral Co centers at the 8*c* site (Figure 1a), while each tetrahedral cobalt node connects to three octahedral linkers. The framework (Figure 1b) of alternating tetranuclear cobalt citrate clusters and tetrahedral cobalt nodes can be described as an infinite 3D (3,6)-connected anatase net (Figure 1c) if the ionic bond is not considered (four K^+ ions occupying the 8*d* position can also be present with the clusters). Replacement of Ti atoms with distorted cuboidal tetranuclear clusters gets rid of the inversion center in the anatase structure, resulting in **1** crystallizing in a lower symmetry space group ($I_4\bar{2}d$) in comparison with anatase ($I4_1/a2/m2/d$). To the best of our knowledge, compound **1** is the first example of MOFs having the anatase topology.

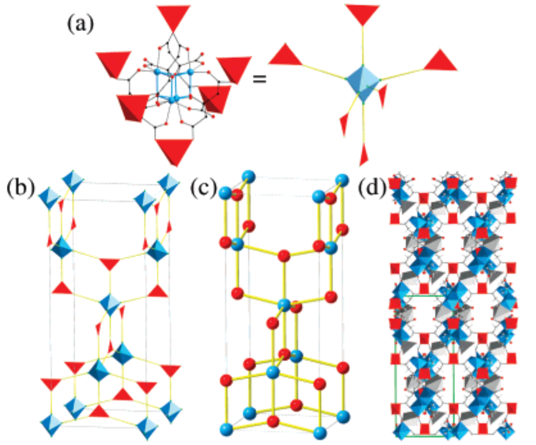

Figure 1. (a) A tetranuclear cluster SBU links six trigonal-node tetrahedral units. Co octahedron, blue; Co tetrahedron, red; O, red; C, black. (b) The topology of the framework of **1** by simplification. Co tetrahedrons, red trigonal nodes; tetranuclear clusters, blue octahedrons. (c) The anatase structure. Ti, blue; O, red. (d) View of **1** along the *a* or *b* axis. K polyhedron, gray; Co polyhedrons, same as those in (a); cell edges, green.

Just like many other metal carboxylate frameworks, the decorated anatase framework is also porous. There are channels along the [1 0 0] and [0 1 0] axes with larger dimensions, ca. 9.5 × 4.3 Å for **1** (Figure 1d), compared with ca. 3.7 × 2.8 Å in anatase. The channels above connect with each other, which produces an intersecting 3D pore occupied by lattice water molecules. To determine the permanent microporosity, the gas sorption isotherm is measured (Figure S7). A plot of weight sorbed per gram of dehydrated **1** vs p/p_0 reveals a reversible type I isotherm. Assuming a monolayer coverage of N_2, the apparent Langmuir surface area is found to be 939 m^2/g with pore volume 0.31 cm^3/g (0.49 cm^3/cm^3). In contrast, for zeolites, apparent surface areas up to 500 m^2/g (Faujasite) and pore volumes up to 0.47 cm^3/cm^3 (zeolite A) have been reported.[15]

The temperature dependence of magnetic susceptibility χ_m for the powder sample of **1** is investigated in the range 2−300 K under 3, 5, and 10 kOe applied fields (Figure 2a). Upon cooling of the sample, $\chi_m T$ basically stays at 8.6 emu K mol^{-1} from room temperature down to 43 K, close to the expected value for three non-interacting Co^{II} centers with $S_i = {}^3/_2$ and an average g value of 2.5.[12a] The behavior is that of a paramagnet with a Weiss constant of +1.4 K for a fit to data taken in 10 kOe field at 50−300 K, indicating that the ferromagnetic interaction between the nearest-neighbor Co atoms (within the Co_4 core) dominates at high temperature.[12a] $\chi_m T$ then declines slowly to down 20 K, followed by an abrupt drop down to 2 K, indicating that there is an

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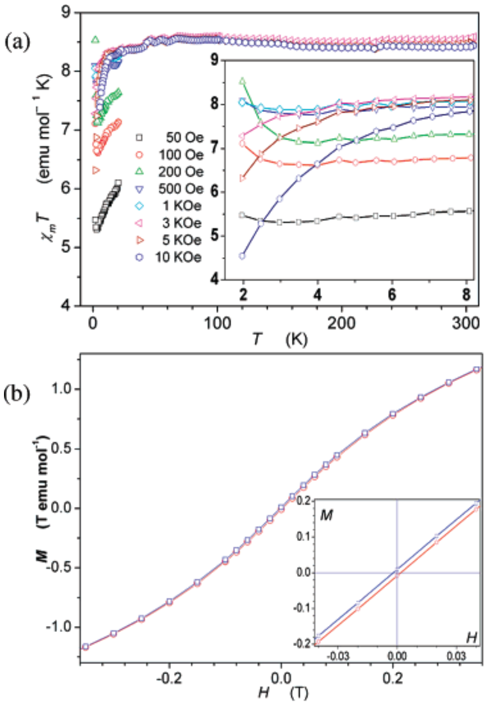

Figure 2. For **1**. (a) Plots of temperature dependence of $\chi_m T$ at 50−10000 Oe field. (b) Hysteresis loop at 2 K.

antiferromagnetic (AF) state for **1** below 43 K. However, $\chi_m T$ at 2−20 K under low field (50−1000 Oe) shows an increase below 5 K, suggesting a ferromagnetic state. The magnetization behavior with the field sensitivity is similar to that for a canted AF cobalt salt under above 1 KOe field.[16] The ac susceptibility shows a nonzero onset of a frequency-dependent out-of-phase signal χ''_m below 5 K with no χ''_m peaks observed above 2 K, indicating a short-range ordering occurrence. The similar χ''_m signal is also seen for the Co_6 cluster below 6 K.[12a] The in-phase $\chi'_m T$ for **1** shows a minimum at 5 K and a frequency dependence at 2 K. Furthermore, a hysteresis loop is observed at 2 K with a coercive field (H_c) of 20 Oe and remnant magnetization (M_r) of 92 Oe emu mol^{-1} (Figure 2b), indicating a magnet-type behavior. Fitting the data in the range ±(4−8) T to eq 1[17] yields a saturated moment M_s (2 K) of $4.98N\beta$,

$$M(H,T) = M_s(T) + \chi_{||}(T)H \qquad (1)$$

which is only half the expected maximum value of $9N\beta$ (this is a characteristic of canted antiferromagnetism[18]) and is larger than the expected minimum value of $3N\beta$ for the ordering with the next-nearest-neighbor AF interaction[19] via a carboxyl group between Co_4 clusters and tetrahedral Co atoms. The canting angle ϕ is 28.9°.[17] The positions of spins within the unit cell show that the stringent symmetry requirements[18] for canted antiferromagnetism (e.g., no inversion center between coupled spins) are met.

Remarkably, these magnetic properties are largely retained by the porous framework of dehydrated **1** (Figure S10). The dc magnetic data in the range 2−20 K under low field show an increase below 5 K. The ac susceptibility shows the onset of a frequency-dependent out-of-phase ac signal χ''_m below 5 K. A hysteresis is also observed at 2 K with H_c of 17 Oe, M_r of 96 Oe emu mol^{-1}, and M_s (2 K) of 35.4 kOe emu mol^{-1}, corresponding to a canting angle ϕ of 35.2°. Thus, dehydrated **1** represents the first metal−organic framework for which microporosity and spin-canted antiferromagnetism coexist although H_c is small.

In summary, the self-assembly[11] of organo-polymetal clusters and metal ions can provide a potential route to magnetic porous metal−organic frameworks. This assembly's merits are obvious:[20] the pore benefits from the big cluster linkers, and the functional framework inherits interesting physical properties from the clusters. Other promising candidates to increase the pore size and to improve the magnetic properties include other analogues of polyoxometalates like Ni_7, Ni_8, Fe_9, and Ni_{21} citrate clusters.[12,13] Ultimately, it is hoped that the realization of such molecules will lead to a material with a highly porous magnetic framework.

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Supporting Information Available: X-ray crystallographic data in CIF format; bond lengths and angles; detailed synthesis process and some supplementary figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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