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Ionothermal Synthesis of Homochiral Framework with Acetate-Pillared Cobalt−Camphorate Architecture

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A new organically templated homochiral material (EMIm)[Co_2(D-cam)$_2$(ac)] (**1**; D-H_2cam = D-camphoric acid; ac = acetate; EMIm = 1-ethyl-3-methylimidazolium) has been ionothermally synthesized, and it features an unusual acetate-pillared cobalt−camphorate architecture encapsulating the cationic component of the ionic liquid.

Homochiral metal−organic frameworks (MOFs) have attracted increasing attention because of their potential applications in asymmetric catalysis and enantioselective separation.[1–3] The use of organic enantiopure chiral building blocks for the construction of extended frameworks has been shown to be a useful method for the synthesis of homochiral materials.[1–4] With few exceptions, known three-dimensional (3D) homochiral MOFs usually have neutral frameworks and occasionally cationic frameworks charge-balanced with simple inorganic anions.[2] In our own work with chiral camphoric acid, all resulting camphorate frameworks found so far are neutral when the syntheses are performed using water or mixed water−alcohol as the solvent.[4a–d] One rare occurrence of the anionic homochiral framework is when a mixture of dimethylformamide (DMF)−alcohol (ethanol or butanol) was used as the solvent.[4e] In this case, the protonated dimethylamine resulting from the decomposition of DMF serves as the cationic structure-directing agent to direct the formation of the homochiral anionic framework. It is worth noting that the anionic framework, while very common in zeolites, phosphates, and many other oxides and chalcogenides,[5,6] only accounts for an unusually small fraction of MOFs. Homochiral anionic MOFs are even rarer.

The synthesis of the homochiral MOFs with the anionic framework, in a way similar to the synthesis of zeolites, could bring new applications associated with the unique compositional and topological features of such materials. The use of DMF for the synthesis of homochiral anionic frameworks mentioned above does not represent a general synthetic method. We are therefore in search of other methods that are generally applicable to different compositional domains. The ionothermal synthesis, which has undergone significant development in the past several years,[7–10] represents a viable option for our purpose. The ionic liquid can serve as both the solvent and the template (sometimes also called a structure-directing agent).[7b] Of particular interest is a recent study by Morris et al. on the use of a chiral ionic liquid to

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induce homochirality in a structure constructed of entirely achiral building blocks.[7d] However, there have been few examples of homochiral MOFs prepared in ionic liquids by using enantiopure structural building blocks.

It is possible to construct 3D homochiral frameworks by cross-linking metal centers with only enantiopure ligands,[4e] however, the number of 3D frameworks that can be produced through this approach has been limited. It can be advantageous to apply a dual-ligand synthetic strategy because the use of two functionally different complementary ligands provides an additional level of control in the framework structure and charge density distribution. One successful dual-ligand synthetic strategy in crystal engineering is to combine a bi- or polydentate carboxylate ligand with a dipyridine ligand.[11] In our earlier work involving chiral camphorates, a common structural mode resulting from the use of this dual-ligand method is that divalent metal cations (or clusters) form neutral chains or sheets with deprotonated chiral comphorates, which are then linked or pillared by auxiliary neutral bipyridine ligands into 3D homochiral frameworks.[4d,f]

In this work, we show that homochiral metal−camphorate layers can also be pillared by the anionic carboxylate ligand. We report here a new homochiral material, (EMIm)[Co_2(D-cam)$_2$(ac)] (**1**; D-H_2cam = D-camphoric acid; ac = acetate; EMIm = 1-ethyl-3-methylimidazolium), which was ionothermally synthesized and features an organically templated 3D framework with a pillared architecture. While it is common for a mononegative acetate ligand to bridge two metal sites, it is quite rare for it to function as pillars between homochiral layers.

The ionothermal reaction of Co(ac)$_2$·6H_2O and D-H_2cam in 1-ethyl-3-methylimidazolium bromide (EMIm-Br) at 120 °C for 7 days generates purple crystals of **1**.[12] The phase purity is supported by powder X-ray diffraction (Figure S1 in the Supporting Information).

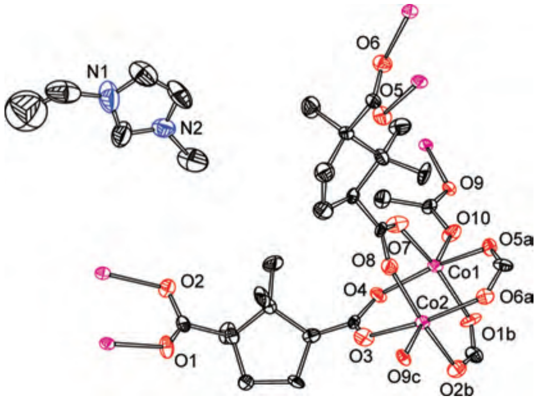

Figure 1. Crystal structure of **1** showing the atom-labeling scheme with 30% probability. H atoms were omitted for clarity. [Symmetry code: (a) $-^1/_2 + x$, $^3/_2 - y$, $-1 - z$; (b) $-^1/_2 + x$, $^1/_2 - y$, $-1 - z$; (c) $-^1/_2 - x$, $1 - y$, $-^1/_2 + z$.]

Single-crystal X-ray diffraction[13] shows that compound **1** crystallized in chiral space group $P2_12_12_1$. The asymmetric unit of **1** contains two Co^{II} ions, two deprotonated D-cam ligands, one deprotonated acetate ligand, and one EMIm ion (Figure 1). The coexistence of the enantiopure ligand D-cam and the achiral ligand acetate in the structure represents an unusual structural mode in homochiral open frameworks. Both Co1 and Co2 sites adopt square-pyramidal geometry. Four carboxylate groups from four D-cam ligands bridge the dinuclear Co centers into a paddle-wheel unit with a metal−metal separation of 2.803 Å. The apical site of each Co center is occupied by one O atom of the pillaring acetate ligand. The Co···O distances range from 2.006(6) to 2.059(7) Å. The cross-linking of adjacent dimers by D-cam ligands leads to a homochiral grid-like (4,4) layered substructure parallel to the *ab* plane (Figure 2a). The auxiliary acetate ligands with the anti−anti conformation serve as pillars to link the [Co(D-cam)]$_n$ layer into an anionic six-connected 3D network (Figure 2b). The Co···Co distance separated by the acetate ligand is 5.991 Å. This noninterpenetrating framework can be simplified into the primitive cubic lattice (denoted: pcu net[14]).

The pillared 3D architecture contains 2D channels parallel to the *ab* plane. The channel along the *a* axis has the dimension of 5.991 × 6.720 Å. The solvent-accessible volume is approximately 1032.1 Å^3 per unit cell volume, and the pore volume ratio is calculated to be 32.8% using the *PLATON* program.[15] The EMIm cations serve as extra-framework guest molecules to fill the void space and charge-balance the anionic framework. It is interesting to note that there are two types of channels along the *b* axis. One is occupied by the EMIm cations, and another is obstructed by the protruding methyl groups of the organic ligands (Figure 3b). The location of the EMIm cation in the channel is also of interest. As shown in Figure 3a, each EMIm cation is located at the center of a four-membered ring formed via four paddle-wheel units, two D-cam ligands, and two ac ligands. The α-methyl groups of two D-cam ligands and two ac ligands all point away from the center of the four-membered ring, which leaves enough space for the EMIm cation.

The thermal behavior of **1** was analyzed on a crystalline sample from 30 to 1000 °C at a heating rate of 10 °C min^{-1}, under a nitrogen atmosphere with a flowing rate of 100 mL min^{-1} (Figure S2 in the Supporting Information). The thermogravimetric curve of **1** is largely unchanged up to 275

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(12) Synthesis of **1**: Co(ac)$_2$·6H_2O (0.3822 g) and D-H_2cam (0.2009 g) in 1-ethyl-3-methylimidazolium bromide (EMIm-Br; 1.848012. g) were mixed in a 23 mL Teflon cup. The vessel was then sealed and heated at 120 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. The purple crystals of **1** were obtained (85% yield based on H_2cam).

(13) Crystal data for **1**: $C_{28}H_{24}Co_2N_2O_{10}$, $M_r = 684.50$, orthorhombic, space group $P2_12_12_1$, $a = 13.3346(10)$ Å, $b = 13.4613(9)$ Å, $c = 17.5115(10)$ Å, $V = 3143.3(4)$ Å^3, $Z = 4$, $D_c = 1.446$ g cm^{-3}, Flack parameter = 0.05(4), R1 (wR2) = 0.0628 (0.1655), and $S = 1.076$ for 4042 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods followed by successive difference Fourier methods. All non-H atoms were refined anisotropically. Computations were performed using *SHELXTL*, and final full-matrix refinements were against F^2.

(14) For definitions of the three-letter abbreviations, see *Reticular Chemistry Structure Resource* (http://rcsr.anu.edu.au/).

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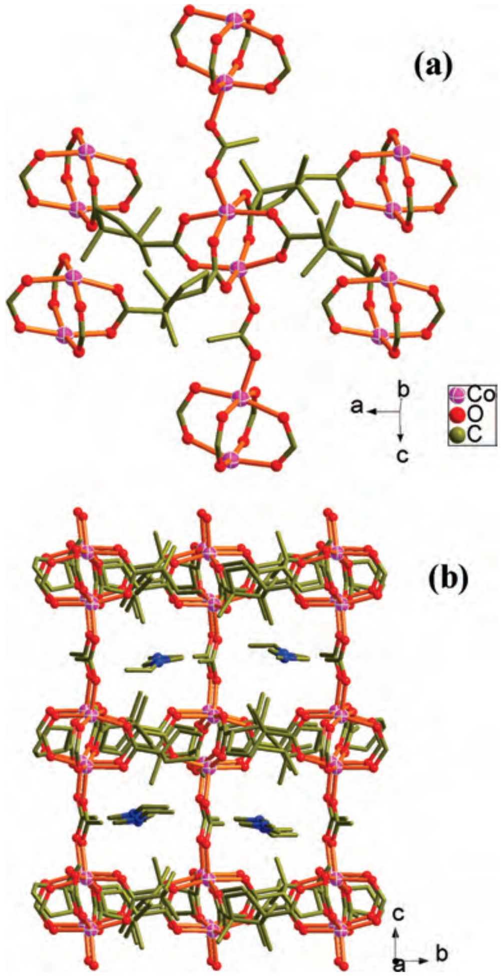

Figure 2. (a) Six-connected paddle-wheel unit in **1**. (b) View of the pillared 3D framework of **1** along the *a* axis, showing channels occupied by the EMIm cations.

°C and then has two steps of weight loss. The first weight loss of 25.2% from 275 to 375 °C corresponds to the loss of the EMIm cations and the ac ligands (calcd 24.9%). The second step from 375 to 515 °C is attributed to the further decomposition of the D-cam ligands. The remaining weight of 22.5% is likely that of CoO (calcd 21.9%).

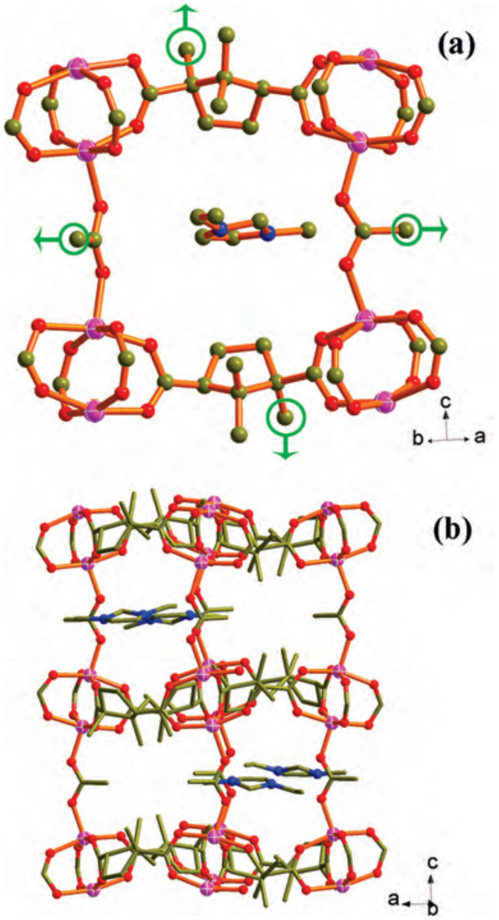

Figure 3. (a) View of the EMIm cation in the four-membered ring (the outside methyl groups are highlighted by green arrows). (b) View of the 3D pillared framework of **1** along the *b* axis, showing two types of channels.

In conclusion, a new anionic homochiral acetate-pillared cobalt−camphorate architecture was successfully prepared under ionothermal conditions through the unique pillaring role of the acetate ligand. The work represents one of few examples of the ionothermal synthesis of homochiral materials using the enantiopure ligand-based building block approach. It combines two of the most rapidly evolving research areas (ionic liquid based materials synthesis and extended homochiral materials) and presents a useful approach that can be further expanded to create a variety of functional materials.

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Supporting Information Available: Powder X-ray diffraction pattern, thermogravimetric analysis diagram, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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