Inorg. Chem. **2008**, *47*, 8607−8609

Inorganic Chemistry
Communication

Cooperative Self-Assembly of Chiral L-Malate and Achiral Succinate in the Formation of a Three-Dimensional Homochiral Framework

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Received July 25, 2008

Chiral L-malate and achiral succinate ligands have been integrated into a three-dimensional homochiral framework by reacting transition-metal cations (Mn^{2+}), L-(−)-malic acid (L-H_2ma), succinic acid (H_2suc), and 4,4′-bipyridine (4,4′-bipy). Chiral L-malate bonds to Mn^{2+} without using the −OH group, which is very unusual for malate. Such unusual bonding of chiral malate results from the cooperative effect of chiral malate and achiral succinate ligands during the self-assembly process, further assisted by the third complementary bipyridine ligand.

Crystalline microporous and open-framework materials with chiral framework are of interest because of their potential applications in enantioselective processes such as catalysis and separation.[1−5] Recent successes with metal−organic framework (MOF) materials have opened up new routes toward the synthesis of homochiral solids because enantiopure organic building blocks can be directly integrated into the framework to generate a homochiral environment.[6−12] However, while this method appears to be conceptually simple, the practical synthesis of bulk homochiral materials remains a significant challenge, as evidenced by the small number of three-dimensional (3D) bulk homochiral materials among numerous known MOF materials.[1−12]

One synthetic strategy that has enjoyed some successes is the use of the dual-ligand approach. In this approach, the formation of neutral homochiral metal carboxylate substructures (e.g., clusters, chains, or sheets) is coupled with cross-linking or pillaring by auxiliary achiral neutral bipyridine ligands, leading to 3D homochiral frameworks.[5a,d]

Here we report a different strategy for the creation of bulk homochiral materials: chirality doping. With this strategy, a chiral carboxylate is used in conjunction with an achiral ligand. With the exception of the chirality property, other features of two ligands are chosen to be as close as possible to promote the integration of two ligands, which will result in the doping of chirality into an otherwise achiral framework.

In this work, to enhance the probability for the formation of a 3D framework (rather than low-dimensional layered or chain-type structures), we combine our chirality doping strategy with the previously used dual-ligand method, which results in a special type of triligand strategy that integrates transition-metal cations, L-(−)-malic acid (=L-H_2ma), suc-

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(1) (a) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217. (b) Guillou, N.; Livage, C.; Drillon, M.; Férey, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5314.

(2) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Lin, Z.; Slawin, A. M. Z.; Morris, R. E. *J. Am. Chem. Soc.* **2007**, *129*, 4880.

(3) (a) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (b) Wu, C.-D.; Lin, W. *Chem. Commun.* **2006**, 3673. (c) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940.

(4) (a) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J.-N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495. (b) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158.

(5) (a) Zhang, J.; Bu, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 6115. (b) Zhang, J.; Chen, S.; Valle, H.; Wong, M.; Austria, C.; Cruz, M.; Bu, X. *J. Am. Chem. Soc.* **2007**, *129*, 14168. (c) Zhang, J.; Liu, R.; Feng, P.; Bu, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 8388. (d) Zhang, J.; Yao, Y.-G.; Bu, X. *Chem. Mater.* **2007**, *19*, 5083. (e) Zhang, J.; Bu, X. *Chem. Commun.* **2008**, 444.

(6) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.

(7) (a) Zheng, S.-T.; Zhang, J.; Yang, G.-Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3909. (b) Liu, G.-Z.; ZHeng, S.-T.; Yang, G.-Y. *Angew. Chem.* **2007**, *46*, 2827. (b) Cheng, J. W.; Zhang, J.; Zheng, S. T.; Zhang, M. B.; Yang, G. Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 73–77.

(8) (a) Forster, P. M.; Eckert, J.; Chang, J.-S.; Park, S.-E.; Férey, G.; Cheetham, A. K. *J. Am. Chem. Soc.* **2003**, *125*, 1309. (b) Guillou, N.; Gao, Q.; Forster, P. M.; Chang, J.-S.; Noguès, M.; Park, S.-E.; Férey, G.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2831.

(9) (a) Chen, B.; Yang, Y.; Zapata, F.; Lin, G.; Qian, G.; Lobkovsky, E. B. *Adv. Mater.* **2007**, *19*, 1693. (b) Chen, B.; Ma, S.; Zapata, F.; Fronczek, F. R.; Lobkovsky, E. B.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 1233. (c) Chen, B.; Ma, S.; Hurtado, E. J.; Lobkovsky, E. B.; Liang, C.; Zhu, H.; Dai, S. *Inorg. Chem.* **2007**, *46*, 8705.

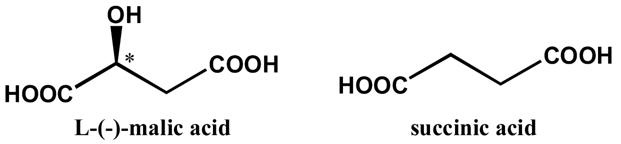
(10) (a) Yang, T.; Sun, J. L.; Eriksson, L.; Li, G. B.; Zou, X. D.; Liao, F. H.; Lin, J. H. *Inorg. Chem.* **2008**, *47*, 3228. (b) Christensen, K. E.; Bonneau, C.; Gustafsson, M.; Shi, L.; Sun, J. L.; Grins, J.; Jansson, K.; Sbille, I.; Su, B. L.; Zou, X. D. *J. Am. Chem. Soc.* **2008**, *130*, 3758. (c) Yang, T.; Ju, J.; Li, G. B.; Liao, F. H.; Zou, X. D.; Deng, F.; Chen, L.; Wang, Y. X.; Lin, J. H. *Inorg. Chem.* **2007**, *46*, 4772.

(11) (a) Attfield, M. P.; Al-Ebini, Y.; Pritchard, R. G.; Andrews, E. M.; Charlesworth, R. J.; Hung, W.; Masheder, B. J.; Royal, D. S. *Chem. Mater.* **2007**, *19*, 316. (b) Harvey, G.; Herve, A. C.; Hailes, H. C.; Attfield, M. P. *Chem. Mater.* **2004**, *16*, 3756. (c) Harvey, G.; Teat, S. J.; Tang, C. C.; Cranswick, L. M.; Attfield, M. P. *Inorg. Chem.* **2003**, *42*, 2428.

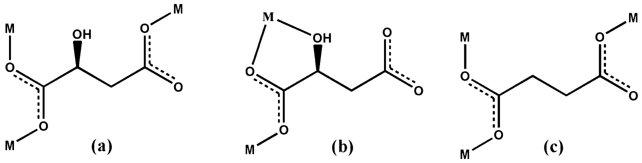
(12) (a) Natarajan, S.; Mandal, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 4798. (b) Mahata, P.; Ramya, K. V.; Natarajan, S. *Chem.−Eur. J.* **2008**, *14*, 5839. (c) Mandal, S.; Natarajan, S. *Inorg. Chem.* **2008**, *47*, 5304.

10.1021/ic801404p CCC: $40.75

Scheme 1. Two Ligands Used for Synthesis



Scheme 2. Two Types of Coordination Modes of the L-ma Ligand Found in **1** (a) and **2** (b), as Well as the Coordination Mode of the suc Ligand Found in **1** (c)



cinic acid (=H_2suc), and 4,4′-bipyridine (=4,4′-bipy) ligands (Scheme 1).

Here we report two homochiral compounds, $[Mn_2(L\text{-}ma)_{0.4}(suc)_{1.6}(4,4'\text{-}bipy)_2(H_2O)_2]\cdot 4,4'\text{-}bipy$ (**1**) and $[Mn(L\text{-}ma)(4,4'\text{-}bipy)(H_2O)]\cdot 3H_2O$ (**2**), which were obtained through the use of the above chirality-doping and triligand strategy.[13] Compounds **1** and **2** were prepared as a mixture from the same synthesis batch. The enantiopure L-malate ligand is incorporated into both frameworks; however, the succinate ligand is only in compound **1**. It is worth noting that L-malate exhibits different coordination modes in two structures. In **2**, L-ma exhibits the commonly observed bonding mode in which its α-hydroxyl group participates in the bonding to metal cations because of the chelating effect involving five-membered rings formed from $-OH$, $-COO^-$, and Mn^{2+} (Scheme 2). In contrast, in compound **1**, L-ma bonds to metal cations using only carboxylate groups. Such a bonding mode is extraordinary for the malate ligand. The unused α-hydroxyl group may provide interesting chemical functionality. Compound **1** is also quite unusual, because it is a very rare homochiral 3D framework that is assembled using three different organic ligands with both similar and complementary features.

Compound **1** crystallizes in the chiral space group $P2_1$ and has a homochiral framework templated by the organic 4,4′-bipy molecules.[14] The dual function of 4,4′-bipy (i.e., cross-linker and extraframework structure-directing agent) is another interesting feature of this work. The most unprecedented structural feature of **1**, however, is the coexistence of the L-ma and suc ligands. In the asymmetric unit of **1**, there are two sites for the carboxylate ligand. One site is occupied by the suc ligand only, while the other site is occupied by 40% chiral L-malate and 60% achiral succinate (Figure 2). To further verify the occupancy, the X-ray data collections were performed with two different crystals. The crystallographic refinement gives the occupancy of L-malate

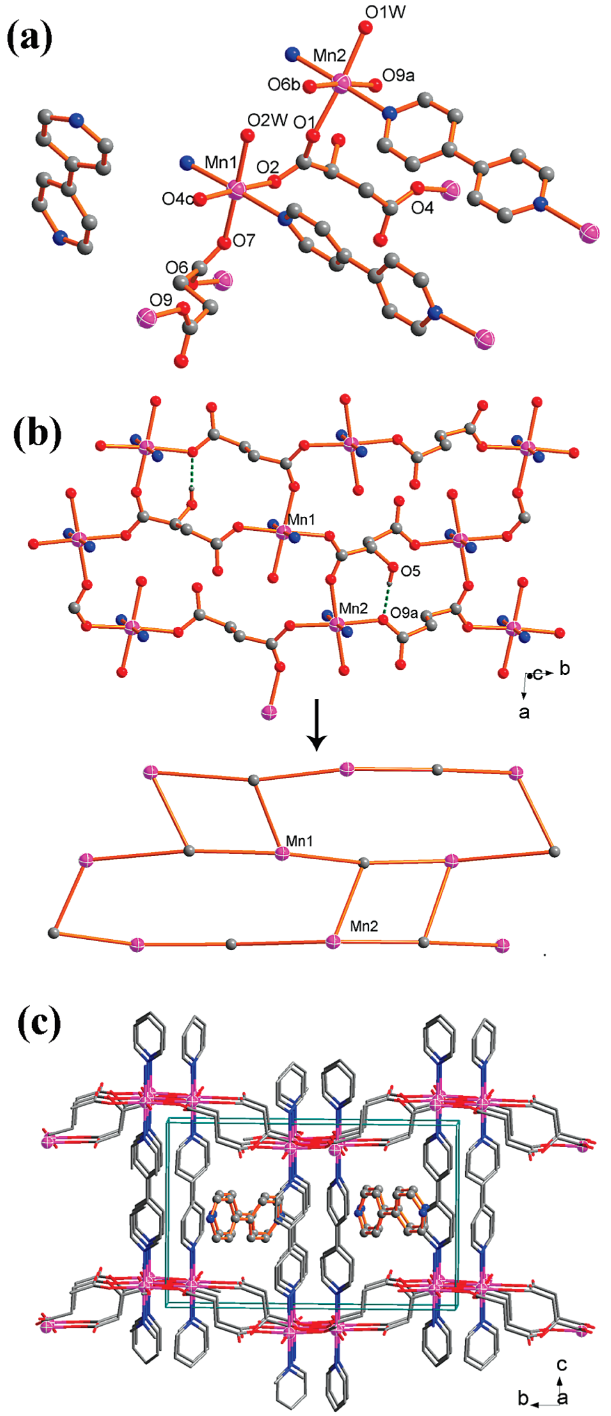


Figure 1. (a) Coordination environment in **1**. (b) Homochiral 2D layer with a 4.8^2 net in **1**, showing the hydrogen-bonding interactions [O−H···O distance = 2.683(13)Å] between the α-hydroxyl O atom (O5) of the L-ma ligand and the carboxylate O atom (O9) of the suc ligand. (c) Homochiral 3D framework of **1**, showing the guest 4,4′-bipy molecules in the ball-and-stick mode.

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(13) Synthesis of $Mn_2(L\text{-}ma)_{0.4}(suc)_{1.6}(4,4'\text{-}bipy)_2(H_2O)_2\cdot bipy$ (**1**) and $Mn(L\text{-}ma)(4,4'\text{-}bipy)(H_2O)\cdot 3H_2O$ (**2**): Manganese nitrate (0.0768 g), sodium carbonate (0.0756 g), L-malic acid (0.0693 g), succinic acid (0.0623 g), 4,4′-bipyridine (0.0802 g), and ethanol (2.0237 g) plus distilled water (2.0185 g) were mixed in a 15-mL glass vial, and the mixture was stirred for 20 min. The vial was then sealed and heated at 120 °C for 5 days. The glass vial was subsequently allowed to cool to room temperature, and crystals formed after 48 h. The final pH was 6.53. Transparent prism-shaped pale-yellow crystals (**1**) and plate-shaped colorless crystals (**2**) were obtained in approximately the same amount.

(14) Crystal data for **1**: $C_{38}H_{36}Mn_2N_6O_{10.4}$, $M_r = 854.61$, monoclinic, space group $P2_1$, $a = 8.8061(3)$ Å, $b = 17.9304(7)$ Å, $c = 11.6984(4)$ Å, $\beta = 100.884(2)°$, $V = 1813.91(11)$ Å^3, $Z = 2$, Flack parameter = 0.02(2), R1 (wR2) = 0.0429 (0.0917), and $S = 1.042$ for 4906 reflections with $I > 2\sigma(I)$. Crystal data for **2**: $C_{14}H_{11}MnN_2O_9$, $M_r = 406.19$, monoclinic, space group $P2_12_12$, $a = 21.6208(4)$ Å, $b = 8.3474(2)$ Å, $c = 11.6482(2)$ Å, $V = 2102.24(7)$ Å^3, $Z = 4$, R1 (wR2) = 0.0773 (0.2223), and $S = 1.067$ for 2704 reflections with $I > 2\sigma(I)$.

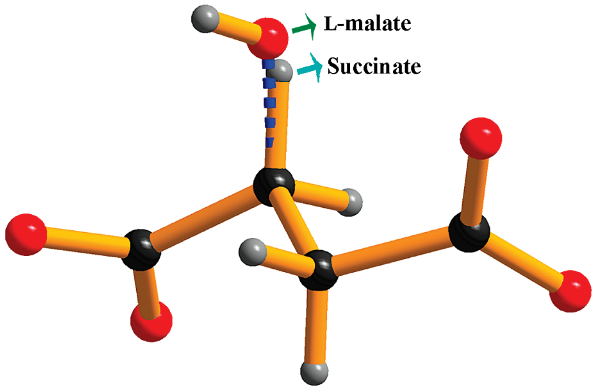

Figure 2. View of the chirality doping through integration of the L-ma ligand at the suc ligand at the same site in **1**.

(measured by the site occupancy of the hydroxyl group) at 39.4% and 39.7%.

As shown in Figure 1a, two crystallographically independent Mn centers have similar $[MnO_4N_2]$ octahedral geometries. However, the Mn1 center is surrounded by two L-ma/L-suc ligands and one suc ligand, and the Mn2 center is surrounded by one L-ma/L-suc ligand and two suc ligands. Notably, the α-hydroxyl group of the L-ma ligand in **1** does not participate in metal−ligand coordination. Only two carboxylate groups of the L-ma ligand coordinate to three Mn centers (Scheme 2). The suc ligand exhibits a μ_3-bridging mode similar to that of the L-ma ligand. These two types of μ_3 linkers connect the Mn centers into a 2D layer parallel to the *ab* plane (Figure 1b). In the layer, the homochiral $[Mn(ma)]_n$ chain and the achiral $[Mn(suc)]_n$ chain are alternately arranged. This layer can be topologically represented as the three-connected 4.8^2 net.

Two-thirds of 4,4′-bipy ligands act as pillars to join $[Mn_2(\text{L-ma})(suc)]_n$ layers into a 3D framework into a previously known topology (Figure 1c).[15] The remaining one-third of 4,4′-bipy ligands serve as the extraframework structure-directing agent.

Compound **2** also crystallizes in the chiral space group $P2_12_12$ and exhibits a hydrogen-bonded network based on 1D homochiral $[Mn(ma)]_n$ connectivity.[14] In **2**, the asymmetric unit contains one Mn atom, one L-ma ligand, one 4,4′-bipy ligand, one aqua ligand, and three guest water molecules (Figure 3a). The Mn ion adopts a distorted octahedral geometry as it coordinates with three O atoms from two individual L-ma ligands, one aqua ligand, and two N atoms from two 4,4′-bipy ligands. The L-ma ligand in **2** is a μ_2 linker with one uncoordinated carboxylate group. It provides one carboxylate O atom (O1) and the α-hydroxyl O atom (O5) to chelate the Mn^{2+} ion and simultaneously uses another carboxylate O atom (O2) to coordinate another Mn^{2+} ion. Such μ_2-bridging L-ma ligands connect the Mn^{2+} ions into a homochiral $[Mn(ma)]_n$ chain along the *b* axis (Figure 3b). The resulting chains are bridged by the 4,4′-bipy ligands via Mn−N coordination, generating a 2D layer parallel to the *bc* plane (Figure 3c).

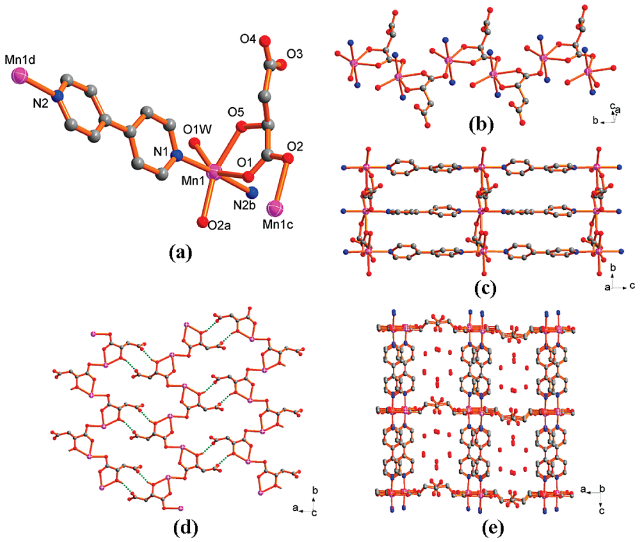

Figure 3. (a) Coordination environment in **2**. (b) Homochiral 1D chain in **2**. (c) 2D layer in **2**. (d) 2D hydrogen-bonded network formed between the Mn(L-ma) chains. (e) 3D packing structure of **2**.

It is interesting to note that the uncoordinated carboxylate group of the L-ma ligand is deprotonated and forms hydrogen bonds with the α-hydroxyl group of another L-ma ligand. Between two L-ma ligands from two adjacent $[Mn(ma)]_n$ chains, two O−H···O hydrogen bonds, with the O···O distance being 2.757 Å, are formed, as shown in Figure 3d. This leads to the formation of the 2D homochiral hydrogen-bonded layer parallel to the *ab* plane. The layers are further pilled up by the 4,4′-bipy ligands, which generates a 3D hydrogen-bonded network with 1D channels along the *b* axis (Figure 3e). The dimensions of each channel are about 9.1 × 11.6 Å^2. The solvent-accessible volume of the main framework is approximately 730.8 Å^3 per unit cell volume, and the pore volume ratio is calculated to be 34.8% using the PLATON program. These channels are filled with guest water molecules.

Acknowledgment. We are thankful for support of this work by the NIH (to X.B. through Grant 2 S06 GM063119-05).

Supporting Information Available: 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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(15) (a) Zheng, Y.-Q.; Lin, J.-L.; Kong, Z.-P. *Inorg. Chem.* **2004**, *43*, 2590. (b) Ma, C.-B.; Chen, F.; Zhang, C.-X.; Hu, M.-Q.; Chen, C.-N.; Liu, Q.-T. *Acta Crystallogr.* **2004**, *C60*, m285.