Inorg. Chem. **2007**, *46*, 8439–8441

Inorganic Chemistry

Communication

$[CH_3NH_2(CH_2)_2NH_2CH_3][M_2(HCOO)_6]$ ($M = Mn^{II}$ and Co^{II}): Weak Ferromagnetic Metal Formate Frameworks of Unique Binodal 6-Connected $(4^{12}\cdot6^3)(4^9\cdot6^6)$ Topology, Templated by a Diammonium Cation

Zheming Wang,*,† Xueyu Zhang,† Stuart R. Batten,*,‡ Mohamedally Kurmoo,*,§ and Song Gao*,†

Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, School of Chemistry, P.O. Box 23, Monash University, Clayton, Victoria, 3800, Australia, and Laboratoire de Chimie de Coordination Organique, CNRS-UMR7140, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, 67000 Strasbourg Cedex 01, France

Received May 13, 2007

Two compounds of $[dmenH_2^{2+}][M_2(HCOO)_6^{2-}]$ ($M = Mn^{II}$ and Co^{II}), synthesized using *N*,*N*′-dimethylethylenediammonium ($dmenH_2^{2+}$) as the template, possess anionic metal formate frameworks of a novel binodal 6-connected $(4^{12}\cdot6^3)(4^9\cdot6^6)$ topology. They are the first coordination examples of this unique network closely related to niccolite and colquiriite and exhibit 3D long-range antiferromagnetic ordering with small spin canting.

Templated synthesis is of great importance in modern chemistry.[1−10] It has been widely used in the syntheses of macrocycles,[2] interlocked species,[3] inorganic materials,[4−8] and even nanomaterials.[7,9] Alkylammonium cations are perhaps the most popular templates. They have been employed in the construction of supramolecular devices and aggregations such as rotaxane/catenane-based molecular machines[10] and have taken critical templating roles in the synthesis of artificial zeolites,[4] metal phosphates,[5] oxometalates,[6] mesoporous MCM-41 class,[7] and metal−organic frameworks such as metal oxalates.[8] The template effects of the ammonium cation lie in (i) the formation of hydrogen bonds between the cation and the templated components, (ii) imprinting, the transfer of the structural information (size and shape) of the cation onto the templated architecture, and (iii) charge compensation. These effects guide the building blocks to form the templated assemblies. Recently, we have investigated the divalent transition-metal formate frameworks templated by alkylmonoammonium cations ($AmineH^+$) and obtained interesting results.[11−13] It is a natural curiosity to see if this approach could be extended to diammonium or polyammonium templates, parallel to the study of metal phosphates and oxometalates.[5,6] We report here the first outcome using *N*,*N*′-dimethylethylenediammonium ($dmenH_2^{2+}$). Interestingly, the two isostructural compounds $[dmenH_2^{2+}][M_2(HCOO)_6^{2-}]$ ($M = Mn^{II}$, **1Mn**; Co^{II}, **2Co**), possess a novel binodal $(4^{12}\cdot6^3)(4^9\cdot6^6)$ framework obviously templated by $dmenH_2^{2+}$, representing the first coordination examples of this unique network topology, and they exhibit weak ferromagnetism.

The two compounds were prepared by the reaction of *N*,*N*′-dimethylethylenediamine (dmen) protonated by formic acid

---

* To whom correspondence should be addressed. E-mail: zmw@pku.edu.cn (Z.W.), gaosong@pku.edu.cn (S.G.), stuart.batten@sci.monash.edu.au (S.R.B.), kurmoo@chimie.u-strasbg.fr (M.K.).

† Peking University.

‡ Monash University.

§ Université Louis Pasteur.

(1) (a) Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *Acc. Chem. Res.* **1993**, *26*, 469. (b) Busch, D. H. *Top. Curr. Chem.* **2005**, *249*, 1.

(2) Laughrey, Z. R.; Gibb, B. C. *Top. Curr. Chem.* **2005**, *249*, 67.

(3) (a) Chichak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S. H.; Cave, G. W. V.; Atwood, J. L.; Stoddart, J. F. *Science* **2004**, *304*, 1308. (b) Dietrich-Buchecker, C.; Colasson, B. X.; Sauvage, J.-P. *Top. Curr. Chem.* **2005**, *249*, 261.

(4) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663.

(5) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.

(6) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(7) de A. A. Soler-Illia, G. J.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093.

(8) Pilkington, M.; Decurtins, S. In *Crystal Design: Structure and Function*; Desiraju, G. R., Ed.; John Wiley & Sons Ltd.: West Sussex, England, 2003; pp 306−310.

(9) van Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980.

(10) (a) Cantrill, S. J.; Pease, A. R.; Stoddart, J. F. *J. Chem. Soc., Dalton Trans.* **2000**, 3715. (b) Schalley, C. A.; Weilandt, T.; Brüggemann, J.; Vötle, F. *Top. Curr. Chem.* **2004**, *248*, 141. (c) Badjić, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845.

(11) (a) Wang, Z. M.; Zhang, B.; Otsuka, T.; Inoue, K.; Kobayashi, H.; Kurmoo, M. *Dalton Trans.* **2004**, 2209. (b) Wang, X. Y.; Gan, L.; Zhang, S. W.; Gao, S. *Inorg. Chem.* **2004**, *43*, 4615.

(12) Wang, Z. M.; Zhang, B.; Inoue, K.; Fujiwara, H.; Otsuka, T.; Kobayashi, H.; Kurmoo, M. *Inorg. Chem.* **2007**, *46*, 437.

(13) (a) Wang, Z. M.; Zhang, Y. J.; Liu, T.; Kurmoo, M.; Gao, S. *Adv. Funct. Mater.* **2007**, *17*, 1523. (b) Wang, Z. M.; Zhang, B.; Zhang, Y. J.; Kurmoo, M.; Liu, T.; Gao, S.; Kobayashi, H. *Polyhedron* **2007**, *26*, 2207 and references cited therein.

10.1021/ic700924j CCC: $37.00 © 2007 American Chemical Society

Published on Web 09/13/2007

with $M(ClO_4)_2·6H_2O$ in methanol.[14] The structure[15] contains one unique formato anion that bridges two unique metal atoms, viz., M1 and M2, and one unique [$dmenH_2^{2+}$] cation (Figures 1 and S1 of the Supporting Information). The *anti*−*anti* formate ligands connect the octahedral metal ions into a 3D framework (Figure 1b), with the [$dmenH_2^{2+}$] cations in its cavities (Figure 1a). The framework can be described as (4, 4) waved sheets parallel to the *ac* plane further linked along the normal direction. In the wavy sheet, M2 atoms lie at the crests and troughs while the M1 atoms lie in the middle. Each M2 in one sheet links two M1 of one neighbor sheet (above or below) in a *cis* mode, while each M1 of one sheet links two M2 from the two neighbor sheets (above and below) in a *trans* mode. The resulting framework is a binodal 6-connected network with ($4^{12}·6^3$)($4^9·6^6$) topology,[16] in which M1 is the ($4^{12}·6^3$) node while M2 is the ($4^9·6^6$) node, and each node links only nodes of the other type (Figure 1b). Such binodal 6-connected networks are rare, with the uninodal α-Po network being the overwhelmingly favored topology for 6-connected networks.[17] In fact, we are unaware of any coordination compound with such a topology.[18] It is noted that the inorganic solids of the niccolite structure (NiAs, containing octahedral Ni and trigonal-prismatic As nodes) have this topology (Figure S2a of the Supporting Information).[19a] It is also interesting that the present frameworks are closely related to another mineral, colquiriite of $LiCaAlF_6$,[19b] in which the Ca^{2+} and Al^{3+} (or Li^+) sites are ($4^{12}·6^3$) and ($4^9·6^6$) nodes, respectively, linked by F^-, if Li^+ (or Al^{3+}) is considered as the cavity cation (Figure S2b of the Supporting Information). The octahedral M1 and M2 show differences in the spatial arrangement of the six neighboring metal sites and the orientation of the six formato ligands (Figure S1 of the Supporting Information). When viewed down the *c* axis, M1 has its six neighboring M2 arranged in an octahedron, and the six formato ligands rotate anticlockwise by their C−H orientation. M2 is surrounded by six neighboring M1 in a trigonal prism, and of the six formato ligands of M2, three are anticlockwise and the other three clockwise. Therefore, M1 and M2 could be referenced to Ni and As nodes in the NiAs net. The two unique M−O distances are M1−O/M2−O = 2.183(2)/2.181(2) Å (**1Mn**) and 2.106(2)/2.104(2) Å (**2Co**). The M···M distances via the formato bridge are 6.103 (**1Mn**) and 5.981 (**2Co**) Å, respectively.

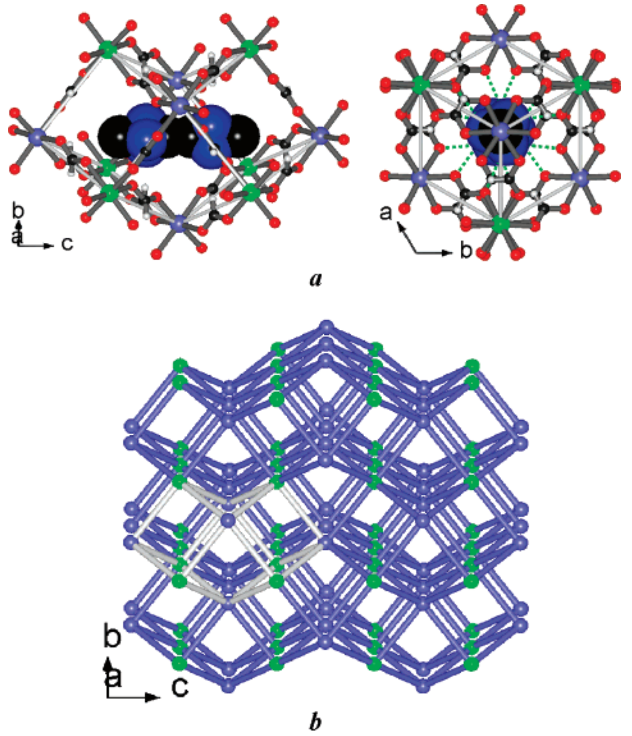

Figure 1. Structure of [$dmenH_2^{2+}$][$M_2(HCOO)_6^{2-}$]. (a) The trigonally disordered [$dmenH_2^{2+}$] cation (space-filling model) within the cavity of the anionic metal formate framework (left, side view; right, top view), with the white sticks emphasizing the cavity. The dashed green bonds in the right-hand figure are N−H···O hydrogen bonds. (b) Topological view of the metal formate framework, with spheres being metal atoms and bonds the *anti*−*anti* HCOO bridges. One cavity is highlighted in white bonds. Color scheme: green, M1 of a ($4^{12}·6^3$) node; light blue, M2 of a ($4^9·6^6$) node; red, O; dark gray or black, C; blue, N; white, H.

The anionic network is templated by [$dmenH_2^{2+}$] (Figure 1a). The cation is trigonally disordered with its two N atoms

---

(14) Preparation. A 0.40 M [$dmenH_2^{2+}$][$HCOO^-$]$_2$ methanol solution was prepared by mixing 0.35 g of dmen and 0.40 g of HCOOH in 10 mL of methanol. A total of 2.0 mL of the [$dmenH_2^{2+}$][$HCOO^-$]$_2$ methanol solution was mixed with 2.0 mL of a 0.20 M methanol solution of the metal salts, $Mn(ClO_4)_2·6H_2O$ for **1Mn** and $Co(ClO_4)_2·6H_2O$ for **2Co**. Microcrystals of **1Mn** (colorless) and **2Co** (pink) were precipitated in 10 min, and then the products were obtained by filtration, washed with methanol, and dried in air. Yields were 93% for **1Mn** and 87% for **2Co** based on metal salts. Powder X-ray diffraction measurements confirmed the phase purity (Figure S6 of the Supporting Information). Crystals suitable for single-crystal X-ray diffraction were obtained by gently mixing 10 mL of a 0.040 M methanol solution of the metal salts with 2.0 mL of a 0.40 M [$dmenH_2^{2+}$][$HCOO^-$]$_2$ methanol solution and leaving the mixture undisturbed for 2 days. Anal. Calcd for **1Mn**, $C_{10}H_{20}Mn_2N_2O_{12}$: C, 25.86; H, 4.31; N, 6.03. Found: C, 25.45; H, 4.30; N, 5.80. Anal. Calcd for **2Co**, $C_{10}H_{20}Co_2N_2O_{12}$: C, 25.10; H, 4.18; N, 5.86. Found: C, 24.94; H, 4.26; N, 5.66.

(15) Characterization. The crystallographic data for the single crystals of **1Mn** and **2Co** were collected at 293 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation of $\lambda = 0.710\,73$ Å. Crystal data for **1Mn**: $M_r = 470.16$, trigonal, space group $P\bar{3}1c$, $a = 8.3176(4)$ Å, $c = 15.0651(5)$ Å, $V = 902.61(7)$ Å^3, $Z = 2$, $D_c = 1.730$ g cm^{-3}, $\mu = 1.462$ mm^{-1}, 10 823 measured data, 692 unique, $R_{int} = 0.0703$. R1 = 0.0318 for 495 observations of $I \geq 2\sigma(I)$, wR2 = 0.0888 for all data, GOF = 0.971. Crystal data for **2Co**: $M_r = 478.14$, trigonal, space group $P\bar{3}1c$, $a = 8.1805(4)$ Å, $c = 14.6798(6)$ Å, $V = 850.77(7)$ Å^3, $Z = 2$, $D_c = 1.866$ g cm^{-3}, $\mu = 2.016$ mm^{-1}, 10 264 measured data, 656 unique, $R_{int} = 0.0863$. R1 = 0.0321 for 459 observations of $I \geq 2\sigma(I)$, wR2 = 0.0818 for all data, GOF = 1.017. CCDC-632132 (**1Mn**) and CCDC-632133 (**2Co**). Powder X-ray diffraction patterns were obtained on a Rigaku RINT2000 diffractometer at room temperature with Cu Kα radiation in a flat-plate geometry. Magnetic measurements were performed on a Quantum Design MPMS 5XL SQUID system for tightly packed polycrystalline samples. Diamagnetic corrections were estimated using Pascal constants (-206×10^{-6} and -202×10^{-6} cm^3 mol^{-1} for **1Mn** and **2Co**, respectively) and background correction by experimental measurement on the sample holder.

(16) (a) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley-Interscience: New York, 1977. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

(17) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176.

(18) A search of the "Reticular Chemistry Structure Resource" website (http://okeeffe-ws1.la.asu.edu/RCSR/home.htm; see ref 17 also) failed to locate this network topology.

(19) (a) West, A. R. *Basic Solid State Chemistry*, 2nd ed.; John Wiley & Sons, Ltd.: Chichester, U.K., 1999. (b) Kuze, S.; du Boulay, D.; Ishizawa, N.; Kodama, N.; Yamaga, M.; Hendersone, B. *J. Solid State Chem.* **2004**, *177*, 3505.

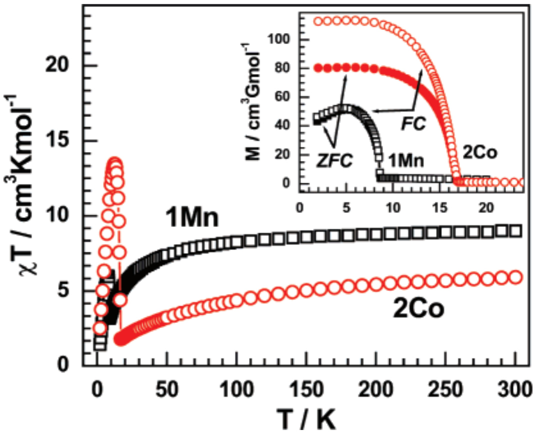

Figure 2. Plots of χT vs T for **1Mn** and **2Co** under a 100 Oe field. Inset: ZFC/FC measurements under a 10 Oe field for **1Mn** and **2Co**.

in six symmetry-related positions. Each N hydrogen bonds to two O atoms of separate formato anions (N1⋯O1/O2 = 2.92−2.94 Å), and each formato anion, in turn, hydrogen bonds to two N positions, one per formato O atom (Figure 1a, right). This is very similar to the hydrogen-bonding pattern in, for example, Stoddart's famous rotaxanes.[10] The cavity can be considered as two one-corner-missing cubanes, twinned together by sharing of the three corners near the missing one. Thus, the cavity is directed by the cation and so is the framework. The template effect was evidenced in the perovskite series of [AmineH$^+$][M(HCOO)$_3^-$] of 6-connected frameworks having the uninodal ($4^{12}{\cdot}6^3$) topology, with the small AmineH$^+$ in the cubic cavity.[11] The smallest ammonium, NH_4^+, led to another 6-connected framework with the rare uninodal ($4^9{\cdot}6^6$) topology.[12] It is worth noting that the [dmenH_2^{2+}] cation results in the current frameworks consisting of both ($4^{12}{\cdot}6^3$) and ($4^9{\cdot}6^6$) nodes. Large, bulky monoammonium cations such as $(CH_3CH_2)_3NH^+$, however, produced the porous diamond frameworks of [$M_3(HCOO)_6$], with open channels occupied by guests that are easily replaced or removed, showing interesting guest-inclusion behavior and guest-induced properties.[13] All of these indicate that metal formate frameworks are very malleable, with the formation of many different network topologies being possible with variation of the size, shape, and hydrogen-bonding geometries of the templating cations. The formation of very unusual network topologies and structures, such as that described here, is also possible using this approach. Similar malleability has already been observed for other systems such as metal dicyanamide frameworks.[20]

The magnetic investigation revealed that **1Mn** and **2Co** are canted antiferromagnets at low temperatures. As shown in Figure 2, upon cooling the χT values (per M_2 unit), starting from 8.99 (**1Mn**) and 5.92 (**2Co**) cm^3 K mol^{-1} at 300 K, decrease continuously and reach minima at 8.7 K (**1Mn**) and 17 (**2Co**) K, then rise sharply to maxima at 7.6 (**1Mn**) and 12.5 (**2Co**) K, and after that they go down to 2 K. The high-temperature susceptibility data obey the Curie−Weiss law (Figure S3 of the Supporting Information) with $C = 9.39$ (**1Mn**) and 7.15 (**2Co**) cm^3 K mol^{-1} and $\Theta = -14.1$ (**1Mn**) and -63.1 (**2Co**) K, respectively. In the low-temperature region, zero-field-cooled and field-cooled measurements (ZFC/FC; Figure 2, inset) indicate the 3D long-range antiferromagnetic ordering with weak ferromagnetism, and the Néel temperatures are 8.5 (**1Mn**) and 16.7 (**2Co**) K, respectively. They are close to that of [AmineH$^+$][M(HCOO)$_3$] with ($4^{12}{\cdot}6^3$) topology[11] and the [NH_4^+][M(HCOO)$_3$] series with ($4^9{\cdot}6^6$) topology,[12] having the same numbers of *anti*−*anti* HCOO links and similar local coordination environments around the metal ions, though the framework topologies are different. The alternating current (ac) susceptibility data and the isothermal magnetization measurement at 2 K (Figures S4 and S5, respectively, of the Supporting Information) further confirm the spin canting in the two materials. The weak ferromagnetism is due to the fact that the structures, with the noncentrosymmtric bridges of *anti*−*anti* HCOO linking metal sites, satisfy the requirement for the antisymmetric interaction,[21] as in other metal formate frameworks.[12,13,22] Finally, the couplings (J/k_B) between M^{II} ions via the formato bridge, estimated from the molecular field result,[23] $J/k_B = 3\Theta/[2zS(S+1)]$, are -0.40 (**1Mn**) and -4.2 (**2Co**) K, agreeable with those metal formate frameworks with *anti*−*anti* HCOO linkages.[12,13,22]

In conclusion, two isostructural compounds of [dmenH_2^{2+}]-[$M_2(HCOO)_6^{2-}$] (M = Mn^{II} and Co^{II}) with metal formate frameworks of a novel binodal 6-connected ($4^{12}{\cdot}6^3$)($4^9{\cdot}6^6$) topology were prepared under the templation of dmenH_2^{2+}. They provide the first examples of this unique network topology in coordination frameworks, and the structures are closely related to niccolite and colquiriite. The two compounds show 3D long-range antiferromagnetic ordering with spin canting arising from the antisymmetric exchange via the noncentrosymmetric HCOO bridge. This work and our previous reports demonstrate that the metal formate coordination polymers display significant malleability and adaptability to templates. Like the metal phosphate or oxometalates, we expect that new metal formate compounds with novel structures and topologies and interesting properties will likely result when different diammonium or polyammonium templates are employed, and this is in progress.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 20571005, 20221101, and 20490210), the National Basic Research Program of China (Grant 2006CB601102), and CNRS, France.

Supporting Information Available: X-ray crystallographic files in CIF format for **1Mn** and **2Co** and a PDF file including Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700924J

---

(20) (a) van der Werff, P. M.; Batten, S. R.; Jensen, P.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **2001**, *40*, 1718. (b) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103.

(21) (a) Dzyaloshinsky, I. *J. Phys. Chem. Solid* **1958**, *4*, 241. (b) Moriya, T. *Phys. Rev.* **1960**, *120*, 91.

(22) See, for example, ref 12 cited in ref 12.

(23) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; p 149.