Inorg. Chem. **2007**, *46*, 5462–5464

Inorganic Chemistry
Communication

Crystal Structures and Magnetic and Ferroelectric Properties of Chiral Layered Metal–Organic Frameworks with Dicyanamide as the Bridging Ligand

Zhi-Guo Gu, Xin-Hui Zhou, Yang-Bo Jin, Ren-Gen Xiong, Jing-Lin Zuo,* and Xiao-Zeng You

Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Received January 22, 2007

Two homochiral 2D-layered frameworks composed of a Cu_2O_2 core and dicyanamide (dca) linkers, $[Cu((R)\text{-hmp*})(dca)]_n$ (**1**) and $[Cu((S)\text{-hmp*})(dca)]_n$ (**2**) (hmp* = α-methyl-2-pyridinemethanol), have been synthesized and structurally characterized. Preliminary investigations suggest that **1** and **2** show possible ferroelectric behaviors. Magnetic studies reveal the existence of strong antiferromagnetic interactions between the Cu^{II} centers in both complexes. The results demonstrate that **1** and **2** are multifunctional material candidates combining ferroelectric and antiferromagnetic properties in one molecule.

Developing new multifunctional materials that display the coexistence or synergism of more than two physical properties in one molecule, such as photomagnetic and magneto-optical materials, chiral magnets, and magnetic conductors, is currently a challenging topic for synthetic chemists.[1] One of the typical examples, ferroelectromagnets combining simultaneous electric and magnetic ordering, not only is of fundamental scientific interest but also is capable of diverse potential applications.[2]

Ferroelectric materials are useful in a variety of new technologies such as ferroelectric random access memories, switchable nonlinear optical devices, electro-optical devices, and light modulators.[3] The synthesis of new ferroelectric materials is particularly challenging because of the strict requirements that a compound needs to crystallize in non-centrosymmetric space groups belonging to the polar point groups. To date, the majority of the ferroelectric materials reported are inorganic compounds such as KH_2PO_4 (KDP), $BaTiO_3$, and $LiNbO_3$.[4] Compared to molecular magnetic materials, the studies on molecular ferroelectric materials from chemists have remained sparse.[5]

The crystal engineering strategy has provided many advantages to constructing chiral or polar supramolecular motifs with optical and magnetic properties.[6] A common approach to ensuring noncentrosymmetric organization in the crystal lattice is insertion of chirality in the molecule. On the basis of this strategy, we obtained two homochiral 2D

---

* To whom correspondence should be addressed. E-mail: zuojl@nju.edu.cn.

(1) (a) Sato, O. *Acc. Chem. Res.* **2003**, *36*, 692. (b) Ohkoshi, S.; Tokoro, H.; Hozumi, T.; Zhang, Y.; Hashimoto, K.; Mathoniére, C.; Bord, I.; Rombaut, G.; Verelst, M.; Cartier dit Moulin, C.; Villain, F. *J. Am. Chem. Soc.* **2006**, *128*, 270. (c) Hozumi, T.; Hashimoto, K.; Ohkoshi, S. *J. Am. Chem. Soc.* **2005**, *127*, 3864. (d) Coronado, E.; Palacio, F.; Veciana, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 2570. (e) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (f) Inoue, K.; Kikuchi, K.; Ohba, M.; Õkawa, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4810. (g) Imai, H.; Inoue, K.; Kikuchi, K.; Yoshida, Y.; Ito, M.; Sunahara, T.; Onaka, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5618. (h) Kaneko, W.; Kitagawa, S.; Ohba, M. *J. Am. Chem. Soc.* **2007**, *129*, 248. (i) Wen, H.-R.; Wang, C.-F.; Li, Y.-Z.; Zuo, J.-L.; Song, Y.; You, X.-Z. *Inorg. Chem.* **2006**, *45*, 7032.

(2) (a) Sott, J. F. *Science* **2006**, *315*, 954. (b) Cui, H. B.; Wang, Z.; Takahashi, K.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **2006**, *128*, 15074. (c) Zheng, H.; Wang, J.; Lofland, S. E.; Ma, Z.; Mohaddes-Ardabili, L.; Zhao, T.; Salamanca-Riba, L.; Shinde, S. R.; Ogale, S. B.; Bai, F.; Viehland, D.; Jia, Y.; Schlom, D. G.; Wuttig, M.; Roytburd, A.; Ramesh, R. *Science* **2004**, *303*, 661. (d) Qi, X.; Zhou, J.; Yue, Z.; Gui, Z.; Li, L.; Buddhudu, S. *Adv. Mater.* **2004**, *14*, 920. (e) Wang, J.; Neaton, J. B.; Zheng, H.; Nagarajan, V.; Ogale, S. B.; Liu, B.; Viehland, D.; Vaithyanathan, V.; Schlom, D. G.; Waghmare, U. V.; Spaldin, N. A.; Rabe, K. M.; Wuttig, M.; Ramesh, R. *Science* **2003**, *299*, 1719. (f) Matsui, T.; Tanaka, H.; Fujimura, N.; Ito, I.; Mabuchi, H.; Morii, K. *Appl. Phys. Lett.* **2002**, *81*, 2764. (g) Kanai, T.; Ohkoshi, S. I.; Nakajima, A.; Watanabe, T.; Hashimoto, K. *Adv. Mater.* **2001**, *13*, 487. (h) Mahesh, M.; Palkar, V. R.; Srinivas, K.; Suryanarayana, S. V. *Appl. Phys. Lett.* **2000**, *76*, 2674. (i) Hill, N. A. *J. Phys. Chem. B* **2000**, *104*, 6694. (j) Lopatin, S.; Lopatina, I.; Lisnevskaya, I. *Ferroelectrics* **1994**, *162*, 63.

(3) (a) Naumov, I. I.; Fu, H. *Phys. Rev. Lett.* **2005**, *95*, 247602. (b) Naumov, I. I.; Bellaiche, L.; Fu, H. *Nature* **2004**, *432*, 737. (c) Ahn, C. H.; Rabe, K. M.; Triscone, J. M. *Science* **2004**, *303*, 488. (d) Junquera, J.; Ghosez, P. *Nature* **2003**, *422*, 506. (e) Fu, H.; Bellaiche, L. *Phys. Rev. Lett.* **2003**, *91*, 257601. (f) Maly, K. E.; Wand, M. D.; Lemieux, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 7898. (g) Lemieux, R. P. *Acc. Chem. Res.* **2001**, *34*, 845. (h) Scott, J. F. *Ferroelectric Memories*; Springer: New York, 2000. (i) Auciello, O.; Scott, J. F.; Ramesh, R. *Phys. Today* **1998**, *51*, 22.

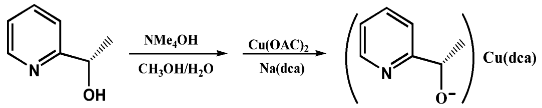
(4) (a) Rijnders, G.; Blank, D. H. V. *Nature* **2005**, *433*, 369. (b) Lee, H. N.; Christen, H. M.; Chisholm, M. F.; Rouleau, C. M.; Lowndes, D. H. *Nature* **2005**, *433*, 395.

(5) (a) Okubo, T.; Kawajiri, R.; Mitani, T.; Shimoda, T. *J. Am. Chem. Soc.* **2005**, *127*, 17598. (b) Qu, Z.-R.; Zhao, H.; Wang, Y.-P.; Wang, X.-S.; Ye, Q.; Li, Y.-H.; Xiong, R.-G.; Abrahams, B. F.; Liu, Z.-G.; Xue, Z.; You, X.-Z. *Chem.—Eur. J.* **2004**, *10*, 53. (c) Zhao, H.; Qu, Z.-R.; Ye, Q.; Abrahams, B. F.; Wang, Y.-P.; Liu, Z.-G.; Xue, Z.; Xiong, R.-G. *Chem. Mater.* **2003**, *15*, 4166.

(6) (a) Kumagai, H.; Inoue, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 1601. (b) Minguet, M.; Luneau, D.; Lhotel, E.; Villar, V.; Paulsen, C.; Amabilino, D. B.; Veciana, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 586. (c) Ohba, M.; Õkawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313. (d) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Murcia-Martínez, A. *Chem.—Eur. J.* **2006**, *12*, 3484.

10.1021/ic070112s CCC: $37.00

Scheme 1



coordination polymers, [Cu((*R*)-hmp*)(dca)]$_n$ (**1**) and [Cu((*S*)-hmp*)(dca)]$_n$ (**2**), using (*R*)-α-methyl-2-pyridinemethanol or (*S*)-α-methyl-2-pyridinemethanol and dicyanamide (dca) as network building blocks, because we know that dca is one of the typical bridging ligands in magnetic materials.[7] Herein, we report the synthesis, solid-state structures, thermal stabilities, and ferroelectric and magnetic properties of the two homochiral frameworks.

Complexes **1** and **2**[8] were obtained as light-blue prism-shaped crystals by the reaction of (*R*)-α-methyl-2-pyridinemethanol or (*S*)-α-methyl-2-pyridinemethanol, Cu(OAc)$_2$·H$_2$O, and Na(dca) in a 1:1:1 molar ratio in a methanol/water mixture at room temperature (Scheme 1). IR spectroscopic analysis of **1** and **2** reveals three intense absorptions at 2173, 2242, and 2327 cm^{-1} corresponding to the combination modes of vibration of the dca anion. Thermogravimetric analysis on polycrystalline samples of complexes **1** and **2** indicated no weight loss up to 200 °C (Figure S1 in the Supporting Information).

Complexes **1** and **2** are enantiomers and are crystallized in the chiral space group ($P2_1$). No detailed structural descriptions are presented here for **2**. X-ray structural analyses of **1** and **2** reveal the formation of 2D-layered structures (Figure 1). The layer of **1** consists of the asymmetric dinuclear unit of [Cu$_2$((*R*)-hmp*)$_2$(dca)$_2$] shown in Figure 2. Each Cu^{II} ion is coordinated to two (*R*)-hmp* ligands as well as to the two N atoms of two dca bridges, forming a distorted square-pyramidal coordination conformation. The basal positions of the square pyramid are occupied by N$_2$O$_2$ atoms with Cu−N bond lengths [1.929(7)−2.002(9) Å] and Cu−O bond lengths [1.881(6)−1.972(5) Å]. Also, the apical position is occupied by the other dicyanamide N atom with a much longer bond length [2.332(7)−2.358(6) Å]. The Cu$_2$O$_2$ core is not planar and folded along the O···O line with the dihedral angles of 16.16°. The Cu−O−Cu bridging angles are in the ranges of 99.0(3)−103.9(3)°. The dca$^-$ ligands bridge neighboring Cu$_2$ units and yield a 2D arrangement of the Cu$_2$ units running in the *ac* plane. The layers repeat in an ···ABCABC··· stacking sequence, and a view from the *b* axis is shown in Figure 3. There are no open channels in the crystal of **1**. The Cu···Cu distances within the layer are 8.505 and 8.565 Å via the dca$^-$ bridges, whereas the nearest interlayer Cu···Cu distance is 5.524 Å.

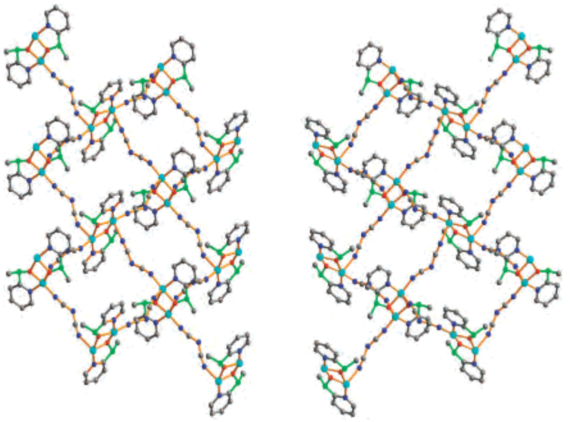


Figure 1. Perspective views of the layered structures of **1** (*R* isomer, left) and **2** (*S* isomer, right). Color code: C, gray; N, dark blue; O, red; Cu, light blue. The green balls represent the chiral centers.

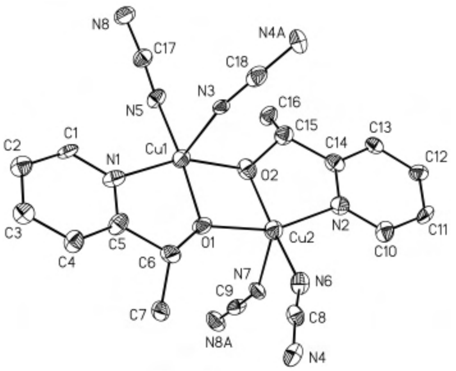


Figure 2. Perspective drawing of complex **1** showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu1−O1 1.881(6), Cu1−O2 1.972(5), Cu1−N1 2.002(9), Cu1−N3 2.358(6), Cu1−N5 1.929(7), Cu2−O1 1.915(5), Cu2−O2 1.957(7), Cu2−N2 1.979(8), Cu2−N6 1.969(7), Cu2−N7 2.332(7); O1−Cu1−O2 77.3(2), O1−Cu1−N3 98.1(2), O1−Cu1−N5 169.4(3), O2−Cu1−N3 93.7(2), O2−Cu1−N5 100.5(3), N3−Cu1−N5 92.4(3), O1−Cu2−O2 76.9(2), O1−Cu2−N6 97.4(3), O1−Cu2−N7 95.9(2), O2−Cu2−N6 165.8(3), O2−Cu2−N7 100.0(2), N6−Cu2−N7 93.5(3), Cu1−O1−Cu2 103.9(3), Cu1−O2−Cu2 99.0(3).

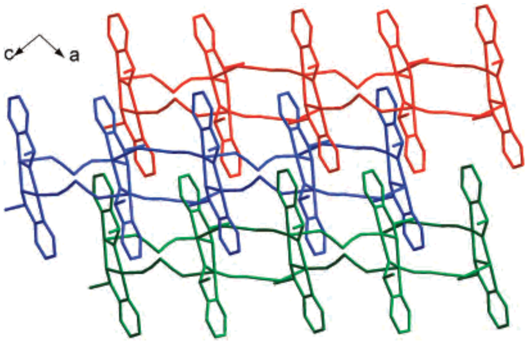


Figure 3. Side view of the three layers of complex **1** in the *ac* plane.

---

(7) (a) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103 and references cited therein. (b) Ortega-Villar, N.; Thompson, A. L.; Carmen Muñoz, M.; Ugalde-Saldívar, V. M.; Goeta, A. E.; Moreno-Esparza, R.; Real, J. A. *Chem.*−*Eur. J.* **2005**, *11*, 5721. (c) Miyasaka, H.; Nakata, K.; Lecren, L.; Coulon, C.; Nakazawa, Y.; Fujisaki, T.; Sugiura, K.-i.; Yamashita, M.; Clérac, R. *J. Am. Chem. Soc.* **2006**, *128*, 3770.

(8) Preparation of complexes **1** and **2**: (*R*)-α-methyl-2-pyridinemethanol (12 mg, 0.1 mmol) and Me$_4$NOH with 25% methanol (36.4 mg, 0.1 mmol) were added to a methanol solution (10 mL) containing Cu(OAc)$_2$·H$_2$O (20 mg, 0.1 mmol). After the solution was stirred at room temperature for 1 h, Na(dca) (8.9 mg, 0.1 mmol) in 5 mL of water was added to the above solution and then further stirred for 2 h. The resulting clear solution was filtered and left to stand at room temperature. Light-blue prisms of **1** suitable for X-ray diffraction were obtained by slow evaporation of the solvents within 1 week. Complex **2** was obtained using a method similar to that of **1**, except that (*S*)-α-methyl-2-pyridinemethanol was used. Yield: 72%. IR (KBr disk): $\nu_{C\equiv N}$ 2173, 2242, and 2307 cm^{-1}. Anal. Calcd for $C_{18}H_{16}Cu_2N_8O_2$: C, 42.94; H, 3.20; N, 22.26. Found: C, 42.68; H, 3.41; N, 22.03. Crystal data for **1**: $C_{18}H_{16}Cu_2N_8O_2$, $M = 503.47$, $T = 293$ K, monoclinic, space group $P2_1$, $a = 7.568(1)$ Å, $b = 15.352(2)$ Å, $c = 8.482(1)$ Å, $\beta = 97.101(2)°$, $V = 997.8(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.710$ g cm^{-3}, $\mu = 2.209$ mm^{-1}, R1 = 0.0592, wR2 = 0.1259 [$I > 2\sigma(I)$] for 3582 data and 271 parameters, $S = 1.001$, Flack parameter $\chi = 0.06(3)$. Crystal data for **2**: R1 = 0.0527, wR2 = 0.1028 [$I > 2\sigma(I)$] for 2801 data and 273 parameters, $S = 1.105$, Flack parameter $\chi = 0.08(2)$.

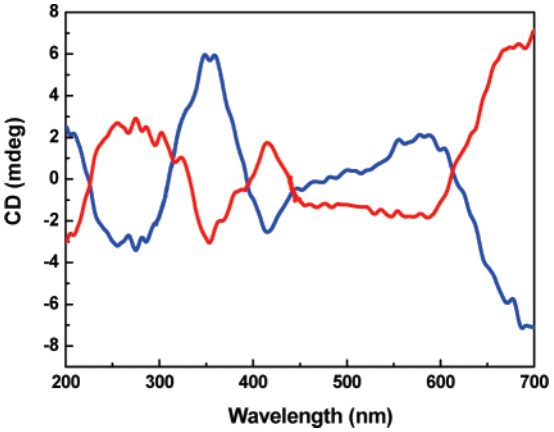


Figure 4. CD spectra of **1** (*R* isomer, blue line) and **2** (*S* isomer, red line) in KBr pellets.

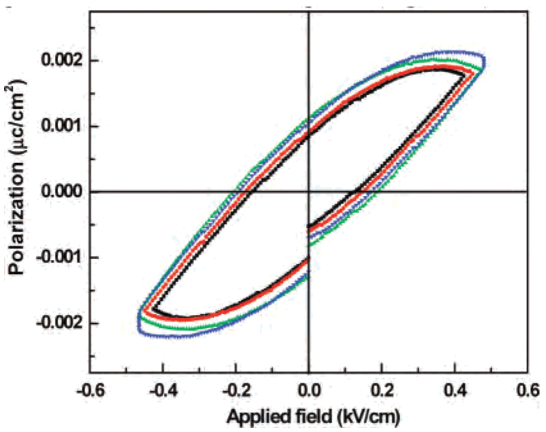


Figure 5. Electric hysteresis loop of a pellet obtained from a powdered sample of **1** observed by virtual ground mode using an RT66 ferroelectric tester at room temperature at different voltages.

The circular dichroism (CD) spectra measured in KBr pellets further confirm the enantiomeric nature of the optically active complexes **1** and **2** (Figure 4). Complex **1** (*R* isomer) exhibits positive Cotton effects at $\lambda_{max} = 354$ and 588 nm and a negative dichroic signal centered at $\lambda_{max} = 274$ and 417 nm, while **2** (*S* isomer) shows Cotton effects of the opposite sign at the same wavelengths.

Given that the products **1** and **2** crystallize in a chiral space group ($P2_1$), their second nonlinear optical properties were studied. The results from the powdered sample indicate that both **1** and **2** are second-harmonic-generation-active with approximate responses of 0.6 times that of urea. Assignment of **1** and **2** to the polar symmetry point group (C_2) implies that **1** and **2** may display potential ferroelectric properties. Figure 5 shows an electric hysteresis loop for **1**, indicating that it exhibits ferroelectric behavior. In comparison, the polarization versus electric field plot for a typical ferroelectric compound, KDP, has been measured under the same experimental conditions as those of complex **1**.

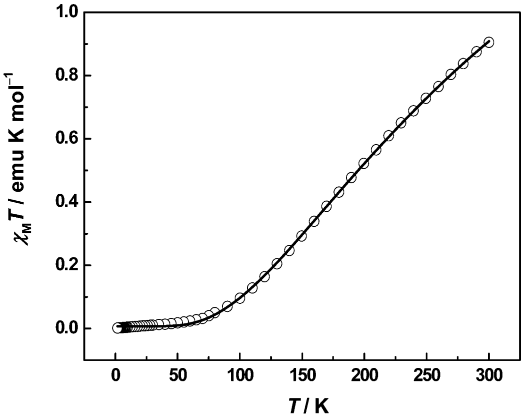


Figure 6. Temperature dependence of the $\chi_M T$ product for **1** at 100 Oe. Solid lines represent the best fitting of the data.

The magnetic susceptibility measurements were performed on polycrystalline samples of complexes **1** and **2** using the SQUID magnetometer at temperatures ranging from 1.8 to 300 K. Because complexes **1** and **2** are a pair of enantiomers, they show the same magnetic behavior. The temperature dependence of the $\chi_M T$ values of **1** is displayed in Figure 6. The value of $\chi_M T$ at room temperature is 0.908 emu K mol^{-1}. As the temperature is decreased, $\chi_M T$ gradually decreases, reaching a plateau value of nearly zero below 80 K and indicating that strong antiferromagnetic couplings between spin centers are operating. According to the structure, **1** can be approximately regarded as a dicopper(II) complex. The data were analyzed using the Bleany−Bowers expression derived from the isotropic spin-exchange Hamiltonian $H = -2JS_1S_2$, where $S_1 = S_2 = {}^1/_2$.[9] The best-fitting results between 1.8 and 300 K with intermolecular interactions (zJ') were obtained: $g = 2.07$, $J = -126.31$ cm^{-1}, $\rho = 0.0088$ (paramagnetic impurity), and $zJ' = -0.47$ cm^{-1} ($R = 2.0 \times 10^{-5}$). As we know, strong to very strong antiferromagnetic spin coupling is very common in similar bisphenoxo-bridged dicopper(II) complexes and the magnitude of the coupling constant J varies from −130 to −509 cm^{-1}.[10]

In summary, two enantiomorphous chiral complexes possessing three properties (ferroelectric, antiferromagnetic, and nonlinear optical) in a simple molecule have been successfully synthesized. Further investigations on chiral α-methyl-2-pyridinemethanol compounds with both ferroelectric and magnetic properties are currently underway in our laboratory. Our target is to prepare ferroelectric ferromagnets from chiral metal complexes, which is an interesting topic for chemists and physicists.

Acknowledgment. This work was supported by the Major State Basic Research Development Program (Grant 2006CB-806104), the National Natural Science Foundation of China, the Program for New Century Excellent Talents in University of China (Grant NCET-04-0469), and the Natural Science Foundation of Jiangsu Province (Grant BK2006512).

Note Added after ASAP Publication. This paper was released ASAP on June 5, 2007 with minor text errors and an incorrect SI file. The correct version was posted on June 8, 2007.

Supporting Information Available: X-ray crystallographic files in CIF format for **1** and **2** and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC070112S

---

(9) Bleany, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

(10) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993; p 160.