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Ferroelectric Heterobimetallic Clusters with Ferromagnetic Interactions

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Two homochiral trinuclear clusters, {$(MeTp)_2Fe_2(CN)_6Ni[(1R,2R)\text{-}chxn]_2$} (**1**) and {$(MeTp)_2Fe_2(CN)_6Ni[(1S,2S)\text{-}chxn]_2$} (**2**) [chxn = 1,2-diaminocyclohexane; MeTp = methyltris(pyrazolyl)borate], have been synthesized and structurally characterized. Ferroelectric and magnetic measurements reveal that they are rare examples of metal−organic compounds bearing ferroelectricity and intramolecular ferromagnetic interactions.

The perpetual trend toward multifunctional and ever-smaller electronic devices has led to the development of new materials with hybridized physical properties. One of the typical examples is multiferroic materials in which both ferromagnetism and ferroelectricity can coexist, and the synergism of these two components may show a giant magnetoelectricity effect.[1] Such multifunctional materials have attracted increasing attention over the past few years owing, in part, to their great potential for application as new types of high-density memory devices that can be electrically written and magnetically read.[1,2] Despite the difficulty in finding materials that are both ferroelectric and magnetic,[3] some pure inorganic compounds such as $RMnO_3$, RMn_2O_5 (R = rare earths), and La_2MMnO_6 (M = Co, Ni, Cu) have been reported to be excellent multiferroic materials.[4] Recently, this research has also been directed toward molecule-based materials, such as metal complexes.[5] Here, organic ligands can be utilized to achieve synthetic flexibility and variation of the metal centers, and their oxidation states can tune physical properties.

On the other hand, many new tricyanometalate-based clusters tailored with organic ligands have been studied recently, and some of them show interesting magnetic behaviors including ferromagnetism and single-molecule magnetism (SMM).[6] If chirality is introduced into these tricyanometallic crystal lattices, the structure may be converted to the highly polarizable system, which is one of the basic requirements for ferroelectricity. Therefore, new types of molecule-based ferroelectric materials with various magnetic properties may be foreseeable. Herein, we report two homochiral trinuclear clusters, {$(MeTp)_2Fe_2(CN)_6Ni[(1R,2R)\text{-}chxn]_2$} (**1**) and {$(MeTp)_2Fe_2(CN)_6Ni[(1S,2S)\text{-}chxn]_2$} (**2**) [MeTp = methyltris(pyrazolyl)borate; (1*R*,2*R*)-chxn = (1*R*,2*R*)-(−)-1,2-diaminocyclohexane; (1*S*,2*S*)-chxn = (1*S*,2*S*)-(+)-1,2-diaminocyclohexane], that exhibit ferroelectricity and ferromagnetism.

The reaction of (1*R*,2*R*)-chxn or (1*S*,2*S*)-chxn with $Ni(ClO_4)_2\cdot 6H_2O$ and $(Bu_4N)[(MeTp)Fe(CN)_3]$ in a mixture of acetonitrile, methanol, and water afforded red-brown block-shaped crystals of **1** and **2**.[7] The samples are verified by powder X-ray diffraction to be a pure phase (Figure S1 in the Supporting Information). The IR spectra for both **1** and **2** show two C≡N stretching absorptions at 2151 and 2124 cm^{-1}, corresponding to bridging and terminal cyanide

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(1) (a) Spaldin, N. A.; Fiebig, M. *Science* **2005**, *309*, 391. (b) Sott, J. F. *Science* **2006**, *315*, 954. (c) Eerenstein, W.; Mathur, N. D.; Scott, J. F. *Nature* **2006**, *442*, 759. (d) Sott, J. F. *Nat. Mater.* **2007**, *6*, 256. (e) Ramesh, R.; Spaldin, N. A. *Nat. Mater.* **2007**, *6*, 21.

(2) Breakthrough of the Year: Areas to Watch. *Science* **2007**, *318*, 1848 (Credit: Livet et. al.).

(3) Hill, N. A. *J. Phys. Chem. B* **2000**, *104*, 6694.

(4) (a) Azuma, M.; Takata, K.; Saito, T.; Ishiwata, S.; Shimakawa, Y.; Takano, M. *J. Am. Chem. Soc.* **2005**, *127*, 8889. (b) Khomskii, D. I. *J. Magn. Magn. Mater.* **2006**, *306*, 1. (c) Cheong, S. W.; Mostovoy, M. *Nat. Mater.* **2007**, *6*, 13. (d) Rao, C. N. R.; Serrao, C. R. *J. Chem. Mater.* **2007**, *17*, 4931. (e) Jiang, Q. H.; Ma, J.; Lin, Y. H.; Nan, C. W.; Shi, Z.; Shen, Z. J. *Appl. Phys. Lett.* **2007**, *91*, 022914.

(5) (a) Cui, H. B.; Wang, Z.; Takahashi, K.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **2006**, *128*, 15074. (b) Ohkoshi, S.; Tokoro, H.; Matsuda, T.; Takahashi, H.; Irie, H.; Hashimoto, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3238. (c) Gu, Z. G.; Zhou, X. H.; Jin, Y. B.; Xiong, R. G.; Zuo, J. L.; You, X. Z. *Inorg. Chem.* **2007**, *46*, 5462. (d) Ye, Q.; Fu, D. W.; Tian, H.; Xiong, R. G.; Chan, P. W. H.; Huang, S. D. *Inorg. Chem.* **2008**, *47*, 772.

(6) For example, see: (a) Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 7656. (b) Wang, S.; Zuo, J. L.; Zhou, H. C.; Choi, H. J.; Ke, Y.; Long, J. R.; You, X. Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 5940. (c) Schelter, E. J.; Prosvirin, A. V.; Dunbar, K. R. *J. Am. Chem. Soc.* **2004**, *126*, 15004. (d) Wang, C. F.; Zuo, J. L.; Bartlett, B. M.; Song, Y.; Long, J. R.; You, X. Z. *J. Am. Chem. Soc.* **2006**, *128*, 7162. (e) Li, D. F.; Parkin, S.; Wang, G. B.; Yee, G. T.; Clérac, R.; Wernsdorfer, W.; Holmes, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 4214. (f) Gu, Z. G.; Liu, W.; Yang, Q. F.; Zhou, X. H.; Zuo, J. L.; You, X. Z. *Inorg. Chem.* **2007**, *46*, 3236.

10.1021/ic801049e CCC: $40.75

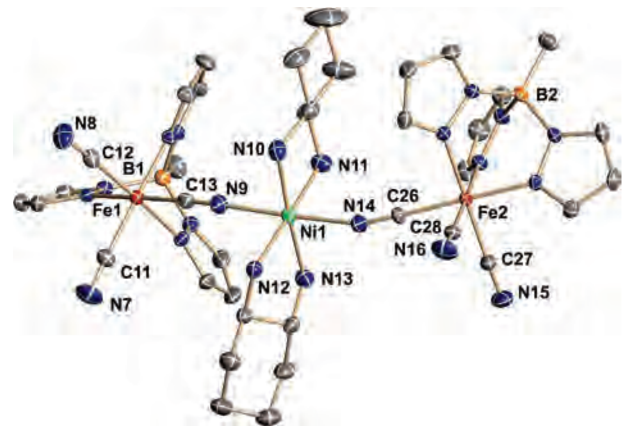

Figure 1. Structure of complex **1**. Thermal ellipsoids are drawing at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **1**: Fe1−C13 1.914(5), Fe2−C26 1.903(6), C13−N9 1.146(7), Ni1−N9 2.105(5), Ni1−N14 2.095(5), Fe1−C13−N9 171.9(5), Fe2−C26−N14 174.8(6), N9−Ni1−N14 177.4(2), Ni1−N9−C13 167.1(5), Ni1−N14−C26 163.0(5).

ligands. The thermogravimetric analysis on a polycrystalline sample of **1** revealed no weight loss up to 230 °C (Figure S2 in the Supporting Information), denoting that the compound is quite stable.

X-ray crystallography reveals that **1** and **2** are enantiomers with a C_2 polar point group (space group $P2_1$), indicating that chirality remains in the solid structures resulting from the chiral diamine ligands.[8] No detailed structural descriptions are presented here for **2** (Table S1 and Figure S3 in the Supporting Information). As shown in Figure 1, complex **1** is a neutral trinuclear Fe_2Ni cluster and a central $\{Ni[(1R,2R)\text{-chxn}]_2\}^{2+}$ core is linked to two $[MeTpFe(CN)_3]^-$ ions at trans positions via bridging cyanides with the Fe−Ni−Fe angle of 162.09(2)°, which is deviating from linearity. The nickel atom is six-coordinated in a distorted octahedral geometry constructed by four nitrogen atoms from two chair (1*R*,2*R*)-chxn ligands and two nitrogen atoms from two cyanide groups. The $Ni-N_{chxn}$ bond distances vary from 2.077(5) to 2.122(5) Å, whereas the $Ni-N_{CN}$ bond lengths are 2.095(5) and 2.105(5) Å. The C≡N−Ni angles [163.0(5)−167.1(5)°] deviate somewhat from strict linearity. Three cyanide ligands in a *fac* arrangement and a tridentate nitrogen-donor MeTp ligand form a distorted octahedral environment around the Fe^{III} ion. The lengths of Fe−C bonds [1.903(6)−1.934(6) Å] and Fe−N bonds [1.960(5)−1.988(4) Å] are in good agreement with those reported previously for structures containing $[(MeTp)Fe(CN)_3]^-$,[9] and the bridging Fe−C≡N angles [171.9(5)−174.8(6)°] are smaller than the terminal ones [175.8(5)−178.8(6)°]. The intramolecular Fe1···Ni1, Fe2···Ni1, and Fe1···Fe2 separations are 5.0969(10), 5.0817(10), and 10.0545(11) Å, respectively, whereas the shortest intermolecular contacts between metal centers are 6.273 Å. Weak hydrogen bonds (N12···N15, 3.090 Å) are observed between the neighboring clusters.

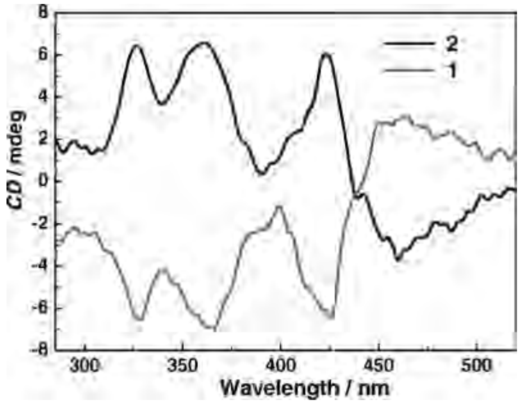

Figure 2. CD spectra of **1** (gray) and **2** (black) in KBr pellets.

To confirm the optical activity and enantiomeric nature of **1** and **2**, the circular dichroism (CD) spectra were measured in KBr pellets. The CD spectrum of **1** exhibits a negative Cotton effect at $\lambda_{max} = 327$, 362, and 423 nm and a positive dichroic signal centered at $\lambda_{max} = 460$ nm, while **2** displays Cotton effects of the opposite sign at the same wavelengths (Figure 2). In addition, the second-order nonlinear optical effect of **1** and **2** was estimated, and they show the second harmonic generation efficiency with a value of 0.8 times that of urea.

The ferroelectric property of **1** was investigated because it crystallizes in a polar point group (C_2) required for ferroelectric behavior. Figure 3 reveals that the complex indeed displays a ferroelectric hysteresis loop with a remanent polarization (P_r) of ca. 0.11−0.32 μC cm^{-2}, which is much larger than that in the previously reported cyano-bridged ferroelectric compound ($P_r \approx 0.041$ μC cm^{-2}).[5b] It shows a coercive field (E_c) of ca. 8.5−20 kV cm^{-1}, and the saturation spontaneous polarization (P_s) is about 0.85 μC cm^{-2}. Additionally, it is observed that both remanent polarization (P_r) and coercive field (E_c) are frequency-dependent, and P_r gradually increases with a decrease in the probing frequencies. This possibly results from the different movability (moving possibility) of the charge carriers with variation of the frequency.[10]

Magnetic measurements were performed on polycrystalline samples of **1** and **2** in the temperature range of 1.8−300 K.

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(7) Preparation of complexes **1** and **2**: A solution of (1*R*,2*R*)-chxn (22.9 mg, 0.2 mmol) in 1 mL of water was added dropwise to a solution of $Ni(ClO_4)_2\cdot 6H_2O$ (36.6 mg 0.1 mmol) in 10 mL of acetonitrile, resulting in the formation of a purple solution. Treatment of this mixture with a solution of $(Bu_4N)[(MeTp)Fe(CN)_3]$ (120.7 mg, 0.2 mmol) in 10 mL of methanol afforded an orange solution, which was filtered and left to stand at room temperature. Red-brown block-shaped crystals of **1** were obtained after 1 week, which were filtered, washed with acetonitrile and ether, and then dried in air. Yield: 67.4 mg, 67% [based on $Ni(ClO_4)_2\cdot 6H_2O$]. Compound **2** was obtained as red-brown block-shaped crystals by a method similar to that of **1**, except that (1S,2*S*)-chxn was used. Yield: 62.8 mg, 62%. Anal. Calcd for $C_{38}H_{52}B_2Fe_2N_{22}Ni$: C, 45.24; H, 5.19; N, 30.54. Found for **1**: C, 45.27; H, 5.11; N, 30.45. Found for **2**: C, 45.37; H, 5.18; N, 30.47. IR (KBr, cm^{-1}): ν_{CN} 2151, 2124. **Caution!** *The perchlorate salts are potentially explosive, so they should be handled in small quantities and with great caution.*

(8) Crystal data for **1**: $C_{38}H_{52}B_2Fe_2N_{22}Ni$, $M = 1009.05$, $T = 291(2)$ K, monoclinic, $P2_1$, $a = 9.1629(8)$ Å, $b = 27.033(2)$ Å, $c = 9.9552(9)$ Å, $\beta = 103.8900(10)°$, $V = 2393.8(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.400$ g cm^{-3}, $\mu = 1.041$ mm^{-1}, R1 = 0.0639, wR2 = 0.1427, $S = 1.098$, Flack $\chi = 0.028(17)$. Crystal data for **2**: $a = 9.1464(14)$ Å, $b = 27.001(4)$ Å, $c = 9.9620(15)$ Å, $\beta = 103.817(2)°$, $V = 2389.1(6)$ Å^3, $\rho_{calcd} = 1.403$ g cm^{-3}, $\mu = 1.043$ mm^{-1}, R1 = 0.0453, wR2 = 0.1119, $S = 1.066$, Flack $\chi = 0.004(13)$.

(9) Wang, C. F.; Liu, W.; Song, Y.; Zhou, X. H.; Zuo, J. L.; You, X. Z. *Eur. J. Inorg. Chem.* **2008**, 717.

(10) Bose, S.; Krupanidhia, S. B. *Appl. Phys. Lett.* **2007**, *90*, 212902.

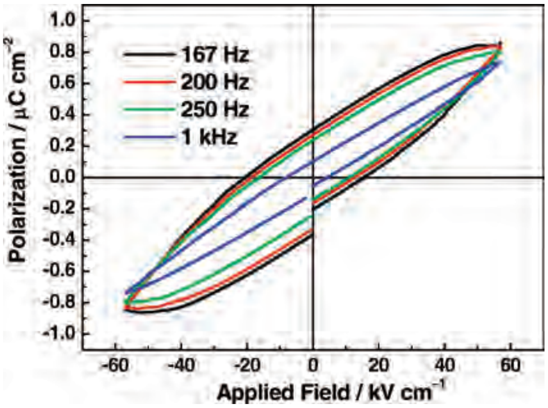

Figure 3. Polarization versus applied electric field at different frequencies (1 kHz to 167 Hz) for **1**. The sample is measured as a pellet-covered silver-conductive glue on a Radiant Technologies Premier Precision II ferroelectric tester at room temperature.

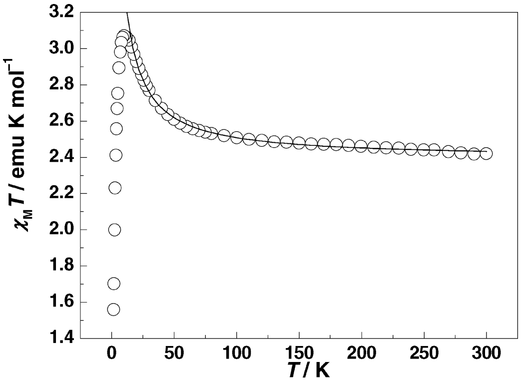

Figure 4. Temperature dependence of $\chi_M T$ for **1** at 2 kOe. The solid line represents the fitting to the data.

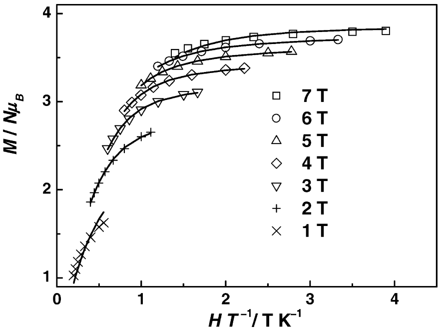

Figure 5. Plot of reduced magnetization, $M/N\mu_B$ (N is Avogadro's number and μ_B is the Bohr magneton), vs H/T for **1**. Solid lines represent fits to the data.

1 and **2** show almost the same magnetic behavior, and only the magnetic properties of **1** are described in detail. The $\chi_M T$ vs T plot for **1** is displayed in Figure 4. The $\chi_M T$ value increases continuously from 2.41 emu K mol^{-1} at 300 K to a maximum of 3.07 emu K mol^{-1} at 10 K with temperature cooling. This suggests ferromagnetic coupling between Fe^{III} and Ni^{II} ions, resulting in an $S = 2$ ground state, which can be further confirmed by the unsaturated magnetization value of 3.87$N\mu_B$ at 7 T (Figure S5 in the Supporting Information). Below 10 K, $\chi_M T$ drops sharply, reaching 1.56 emu K mol^{-1} at 1.8 K, which could be attributed to the zero-field splitting and/or weak intermolecular antiferromagnetic interactions. According to the structure, the Hamiltonian of **1** can be described as $\hat{H} = -2J(\hat{S}_{Fe1}\cdot\hat{S}_{Ni1} + \hat{S}_{Fe2}\cdot\hat{S}_{Ni1})$, which includes only nearest-neighbor exchange (J), and the Van Vleck expression can be written as eq 1.

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\,\frac{1 + 5e^{2J/kT} + e^{-2J/kT}}{3 + 5e^{2J/kT} + 3e^{-2J/kT} + e^{-4J/kT}} \qquad (1)$$

The $\chi_M T$ data were fitted above 16 K to give $g = 2.34$ and $J = +2.91$ cm^{-1} ($R = 9 \times 10^{-5}$), confirming ferromagnetic coupling within the Fe$_2$Ni cluster. The magnitude of exchange coupling is rather weak, which might be attributed to the bent cyanide bridges, and it is comparable to those previously observed for other complexes containing bent Fe^{III}−CN−Ni^{II} linkages.[6e,f,9,11] The magnetization variation for **1** at different magnetic fields was recorded between 1.8 and 5 K (Figure 5). The nonsuperposition of the isofield lines indicates the presence of significant zero-field splitting. With the spin ground state $S = 2$, fits of the magnetization data using the ANISOFIT program[12] afford a zero-field-splitting parameter of $D = -2.09$ cm^{-1} with $g = 2.10$. Although the sign of the fitted D parameter may be not reliable, the fitting result suggests large magnetic anisotropy in **1**. Above 1.8 K, slow paramagnetic relaxation is not observed from alternating current magnetic susceptibility studies under a 5 Oe oscillating field at frequencies up to 1488 Hz.

In conclusion, two homochiral trinuclear heterobimetallic clusters have been successfully synthesized. They display dominant ferromagnetic interactions with large uniaxial magnetic anisotropy; more importantly, they are ferroelectric at room temperature, suggesting that they are rare examples of metal−organic compounds bearing ferroelectricity and intramolecular ferromagnetic interactions. In single-molecular magnets, there is fairly weak intermolecular interaction and they may be more electrically insulating compared to high-dimensional ferro- or ferrimagnets. Our future efforts will therefore focus on the assembly of multiferroic molecule-based materials where ferroelectricity and SMM or single-chain magnet (SCM) behavior coexist.

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Supporting Information Available: Additional characterization data (PDF) and an X-ray crystallographic file (CIF). The material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) Yang, J. Y.; Shores, M. P.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2003**, *42*, 1403. (b) Berlinguette, C. P.; Galán-Mascarós, J. R.; Dunbar, K. R. *Inorg. Chem.* **2003**, *42*, 3416. (c) Li, D. F.; Clérac, R.; Parkin, S.; Wang, G. B.; Yee, G. T.; Holmes, S. M. *Inorg. Chem.* **2006**, *45*, 5251. (d) Liu, W.; Wang, C. F.; Li, Y. Z.; Zuo, J. L.; You, X. Z. *Inorg. Chem.* **2006**, *45*, 10058.

(12) Shores, M. P.; Sokol, J. J.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2279.