Chiral Effects on Magnetic Properties for Chiral and Racemic W^{V}–Cu^{II} Prussian Blue Analogues

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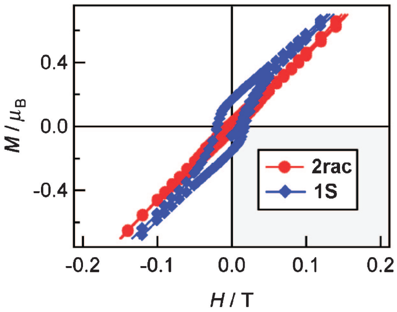

The chiral and racemic 2-D antiferromagnets based on a cyano-bridged W^{V}–Cu^{II} compound are made. Both compounds are almost the same crystal structure, but some differences in magnetic properties appear owing to the existence of the Dzyaloshinsky–Moriya interactions, that is generated by chirality.

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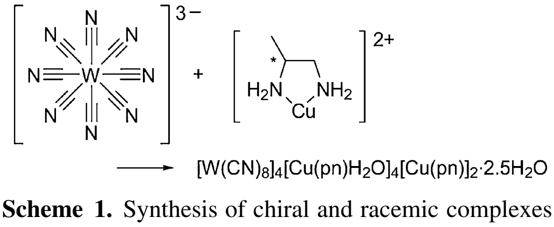
The chiral and racemic 2-D antiferromagnets based on a cyano-bridged W^V–Cu^{II} compound are constructed. Both compounds are similar crystal structure, but some differences in magnetic properties appear owing to the existence of the Dzyaloshinsky–Moriya (DM) interactions,[1] that is generated by crystal chirality.

Molecule-based magnets have attracted much attention for several decades. When the molecular structures are chiral,[2] the chiral magnetic structures are highly expected by the DM interactions. In addition, chiral magnets are expected to show such new phenomena as the magnetization-induced second harmonic generation (MSHG) and magneto-chiral dichroism (MChD).[3] These phenomena originate from the interplay of crystallographic and magnetic chirality. The crystallographic chirality triggers the monoaxial DM vector and stabilizes chiral spin structure. Normally, the origin of the DM interaction is the spin–orbit coupling. The strengths of the third and forth row transition metal ions are larger than those of the second row transition metal ions. By this reason, we use W^V and Cu^{II} to construct a new chiral magnet.[4]

In this paper, we discuss preparation, structure, and magnetic behavior of newly obtained molecule-based chiral and racemic antiferromagnets containing W–Cu; $[W(CN)_8]_4$-$[Cu\{(S\text{ or }R)\text{-pn}\}H_2O]_4[Cu\{(S\text{ or }R)\text{-pn}\}]_2\cdot 2.5H_2O$ (**1S**: S isomer or **1R**: R isomer); ((*S* or *R*)-pn = (*S* or *R*)-1,2-diaminopropane), $[W(CN)_8]_4[Cu\{(rac)\text{-pn}\}H_2O]_4[Cu\{(rac)\text{-pn}\}]_2\cdot 2.5H_2O$ (**2rac**).[5]

Complexes **1S**, **1R**, and **2rac** were obtained as dark purple rhomboid-shaped crystals by the reaction between $Cs_3[W(CN)_8]\cdot 2H_2O$,[6] $CuSO_4\cdot 5H_2O$, and 1,2-diaminopropane ((*S* or *R*)-pn or (*rac*)-pn, respectively) in a 1:1:1 molar ratio in H_2O and stand overnight at room temperature (Scheme 1). The number of water of crystallization can be controlled from 8 to 0. And in our experimental environment, the number of water molecules 6.5 in molecular unit is most stable (See SI).[7] X-ray crystallographic measurements at 200 K revealed that **1S**, **1R**, and **2rac** belong to the space group $P2_1$, $P2_1$ and $P2_1/c$, respectively (Figure 1). The structures are similar but **2rac** has a glide plane and an inversion center, and pn ligands are disordered ((*R*)-pn:(*S*)-pn = 1:1). The chirality of these compounds measured by CD and MCD spectra. **1S** and **1R** show the CD and mirror image each other, and **2rac** does not show the CD signals (see SI).[7]



Scheme 1. Synthesis of chiral and racemic complexes.

The coordination geometry around W^V ion has square-antiprism structure. Five CN groups in $[W(CN)_8]^{3-}$ ion are bridged to Cu^{II} ion, and three other CN groups are free. All Cu^{II} ions have octahedral coordination geometry. There are two different types of the Cu^{II} ions; one is chelated by (*R* or *S*)-pn molecule and coordinated by four CN groups (type A), and the other one is chelated by (*R* or *S*)-pn molecule and coordinated by one water molecule and three CN groups (type B). The interlayer distances are 6.73 and 7.04 Å for **1S**, and 6.87 and 7.08 Å for **2rac**.

The magnetic behavior of compounds was measured by a SQUID magnetometer in the temperature range of 2–300 K and magnetic field range of 0–5 T.[8] **1R** and **1S** have the same magnetic behavior. From now on, we show the **1S** data. All data were taken in powder samples. The $\chi_m T$ values at 300 K are 3.75 emu K mol^{-1} for **1S** and 3.74 emu K mol^{-1} for **2rac**.[7] These values are in good agreement with spin only values, 3.76 emu K mol^{-1} (calculated by using $g = 2$). The $\chi_m T$ values increase up to 27.1 emu K mol^{-1} for **1S** at 8.2 K and 34.5 emu K mol^{-1} for **2rac** at 7.2 K, and decrease by further cooling. The field cooled (FC) and the zero field cooled (ZFC) magnetizations of **1S** and **2rac** in 200 Oe are shown in Figure 2. A long range magnetic ordering is observed at 8.5 K for **1S** and at 7.5 K for **2rac**. The field dependences of the magnetization values at 5 K for **1S** and **2rac** are shown in Figure 3. The saturated magnetization values of both compounds are 9.6 μ_B at 5 T. These values are in good agreement with the saturated moment obtained by considering ferromagnetic coupling between W^V and Cu^{II} ions ($1/2 \times 4 + 1/2 \times 6$). The hysteresis loop in small field is shown in the inset of Figure 3. The H_C values are 186 Oe for **1S** and 52 Oe for **2rac**.[9]

We found a clear difference in magnetizaion between the chiral and racemic compounds. The chiral compound exhibits antiferromagnetic ordering with canting, though the racemic compound exhibits antiferromagnetic ordering without canting. The 2_1 axis is parallel to *b* axis, then structurally screw axis is *b* axis. The spins of the chiral compound canted by the nonzero DM vectors. Based on the group-theoretical consideration, the nonzero DM vectors are induced along the *b* axis. Therefore, the *b* axis is expected to become a magnetic screw axis. The spin canting angle α is 9.97×10^{-3} rad (0.571°). At present, it is not so clear whether the magnetic structure of the chiral compound

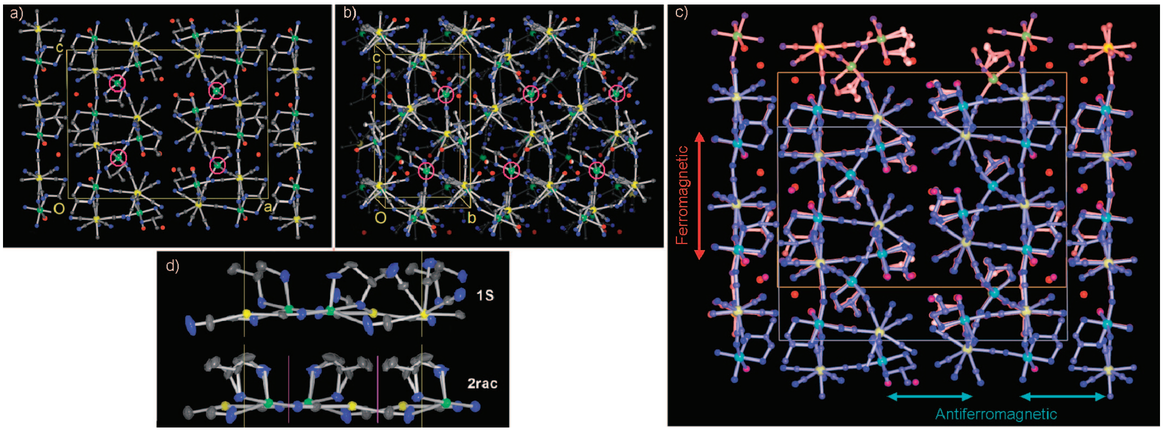


Figure 1. X-ray crystal structures of **1S**; view along a) *b* axis and b) *a* axis. C (gray), Cu (green), N (blue), O (red), and W (yellow). Copper ions marked by pink circles have no water (type A) (see text). c) Superimposed views of **1S** (blue) and **2rac** (red) samples. d) The chiral ligands ORTEP picture for **1S** and **2rac**. The pink line is glide plane. The C atoms of pn are disordered and each occupancies are 0.5.

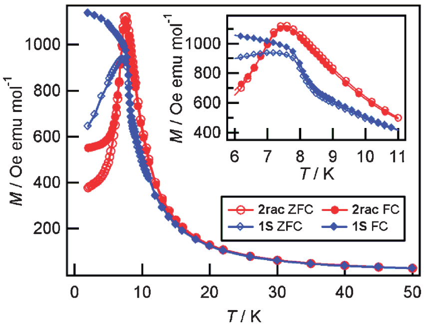


Figure 2. The ZFC and FC (200 Oe) magnetization of **1S** (◆) and **2rac** (●) powder samples.

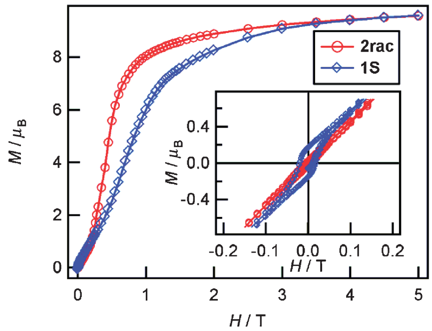


Figure 3. The field dependence of the magnetization for **1S** (◆) and **2rac** (●) powder samples.

has chiral helical/conical or simple canted-antiferromagnetic spin structure. To make this point clear, we need to prepare single-crystal samples and perform neutron diffraction and/or μSR measurements.

In conclusion, we have successfully constructed the cyano-bridged chiral and racemic W^{V}–Cu^{II} compounds. We found that the structural difference gives rise to essentially different magnetizaion profiles. The chiral compound exhibits antiferromagnetic ordering with canting, but the racemic compound exhibits antiferromagnetic ordering without canting. This difference is clearly understood based on the presence or absence of the DM vectors. In the chiral compound, the space group $P2_1$ admits the presence of the DM vectors. Asymmetric electronic dipole fields, which come from asymmetric space group, generate the DM vectors (See SI).[7] Our findings clearly manifest the interplay of crystallographic chirality and the magnetic structure.

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References and Notes

1 M. J. Freiser, *Phys. Rev.* **1961**, *123*, 2003; L. L. Liu, *Phys. Rev. Lett.* **1973**, *31*, 459; A. N. Bogdanov, U. K. Rößler, M. Wolf, K.-H. Müller, *Phys. Rev. B* **2002**, *66*, 214410; J. Kishine, K. Inoue, Y. Yoshida, *Prog. Theor. Phys. Suppl.* **2005**, *159*, 82.

2 A. Caneschi, D. Gatteschi, P. Ray, R. Sessoli, *Inorg. Chem.* **1991**, *30*, 3936; H. Kumagai, K. Inoue, *Angew. Chem., Int. Ed.* **1999**, *38*, 1601; K. Inoue, H. Imai, P. S. Ghalsai, K. Kikuchi, M. Ohba, H. Okawa, J. V. Yakhmi, *Angew. Chem., Int. Ed.* **2001**, *40*, 4242; R. Andrés, M. Brissard, M. Gruselle, C. Train, J. Vaissermann, B. Malézieux, J.-P. Jamet, M. Verdaguer, *Inorg. Chem.* **2001**, *40*, 4633; K. Inoue, K. Kikuchi, M. Ohba, H. Ōkawa, *Angew. Chem., Int. Ed.* **2003**, *42*, 4810; H. Imai, K. Inoue, K. Kikuchi, Y, Yoshida, M. Ito, T. Sunahara, S. Onaka, *Angew. Chem., Int. Ed.* **2004**, *43*, 5618; H. Imai, K. Inoue, K. Kikuchi, *Polyhedron* **2005**, *24*, 2808; E. Coronado, C. J. Gómez-García, A. Nuez, F. M. Romero, J. C. Waerenborgh, *Chem. Mater.* **2006**, *18*, 2670.

3 G. L. J. A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493; H. Tachibana, H. Kishida, Y. Tokura, *Appl. Phys. Lett.* **2000**, *77*, 2443.

4 R. Podgajny, T. Korzeniak, M. Balanda, T. Wasiutynski, W. Errington, T. J. Kemo, N. W. Alcock, B. Sieklucka, *Chem. Commun.* **2002**, 1138; S. Ohkoshi, Y. Arimoto, T. Hozumi, H. Seino, Y. Mizobe, K. Hashimoto, *Chem. Commun.* **2003**, 2772; T. Korzeniak, K. Stadnicka, M. Rams, B. Sieklucka, *Inorg. Chem.* **2004**, *43*, 4811; T. Korzeniak, K. Stadnicka, R. Pelka, M. Balanda, K. Tomala, K. Kowalski, B. Sieklucka, *Chem. Commun.* **2005**, 2939; Y. S. You, J. H. Yoon, J. H. Lim, H. C. Kim, C. S. Hond, *Inorg. Chem.* **2005**, *44*, 7063.

5 The racemic compound, **2rac** is already synthesized and published: D. Li, L. Zheng, X. Wang, J. Huang, S. Gao, W. Tang, *Chem. Mater.* **2003**, *15*, 2094. This article reported the racemic compound as $[W(CN)_8][Cu\{(rac)\text{-}pn\}H_2O]_4[Cu\{(rac)\text{-}pn\}]_2 \cdot 2H_2O$. The number of water of crystallization is different from **2rac** but the number can be controlled (see SI).

6 L. D. C. Bok, J. G. Leipoldt, S. S. Basson, *Z. Anorg. Allg. Chem.* **1975**, *415*, 81.

7 Supporting Information is available electrically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

8 The magnetic behaviors were measured carefully; the fresh samples were put in a sample space is kept at low temperature. Diamagnetic corrections were estimated from Pascal’s Tables.

9 H. Imai, K. Inoue, K. Kikuchi, *Polyhedron* **2005**, *24*, 2808.

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