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Crystal-to-Crystal Transformation from Antiferromagnetic Chains into a Ferromagnetic Diamondoid Framework

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The application of crystal-to-crystal transformations involving dimensionality changes of coordination polymers to generate dynamic magnetic systems is currently a challenging topic in molecular materials research. Although a few crystal-to-crystal transformations have been reported in recent years, very few examples involving crystal-to-crystal transformations exhibiting drastic changes in magnetic properties are known.[1] It is usually difficult to obtain high-quality transformed crystals after removal of the bonded waters or solvents because of the collapse of the framework.[2] Herein, we present two new compounds, $CoCl_2$(1,4-dioxane)$(H_2O)_2$ (**1**) and $CoCl_2$(1,4-dioxane) (**2**), which undergo a crystal-to-crystal transformation from 1D chains in **1** into a 3D diamondoid network in **2** accompanied by a drastic change in magnetic properties.

There are two methods for obtaining compounds **1** and **2**. One is the solvothermal method, through which **1** and **2** can be obtained separately. The other is the hydration/dehydration method. Crystals of **1** allowed to dehydrate in dry air or at elevated temperatures undergo a transformation to yield **2**, and conversely, crystals of **2** allowed to hydrate in wet air can also be transformed into **1**. These transformations were confirmed by powder X-ray diffraction [see the Supporting Information (SI)]. The crystal color, structure (shown in Figure 1), and cell parameters of **1** and **2** are different.

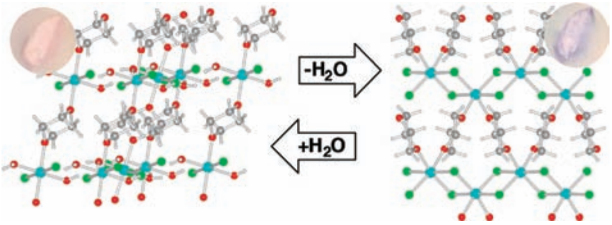

Figure 1. Crystal structures and appearances of **1** and **2**. Color code: Co, blue; C, gray; O, red; Cl, green; H, light gray. Hydrogen bonds in **1** have been omitted for clarity.

1 consists of neutral chains of $CoCl_2$(1,4-dioxane)$(H_2O)_2$ along the *a* axis. Within the chain, the Co^{2+} ions are bridged by 1,4-dioxane molecules in the chair conformation, as in $ZnCl_2$(1,4-dioxane)$_2$ and $ZnBr_2$(1,4-dioxane).[3] Each unique Co^{2+} is octahedrally coordinated by two Cl^-, two H_2O, and two O atoms (one from each of two 1,4-dioxane molecules) trans to each other. There are hydrogen bonds between the H_2O molecules and Cl^- on neighboring chains (O1−H3···Cl1, 2.29 Å/166°; O1−H5···Cl1, 2.26 Å/164°). The shortest intrachain Co−Co distance is 6.859 Å, and the shortest interchain distance is 6.132 Å.

The diamondoid framework of **2**, with nodes of Co-centered $CoCo_4$ tetrahedra, differs from that of the previously reported MCl_2(1,4-dioxane) systems.[3a,4] In each tetrahedron, a Co ion is located at the center and at each of the apexes (Figure S6 in the SI). By sharing metal apexes, these tetrahedra form a diamondoid framework in which all of the metal atoms possess octahedral coordination geometry. This feature is similar to what is observed in $CdCl_2(C_4H_8N_2)$, $CdBr_2(C_4H_8N_2)$ and porous magnetic $Mn_3(HCOO)_6$.[1a,5] Each unique Co^{2+} is octahedrally coordinated by four Cl^- ions and one O atom from each of two 1,4-dioxane molecules. Cl^- ions bridge neighboring Co ions to form a $CoCl_2$ zigzag chain along the *c* axis. The Co−Cl−Co angle of 93.70° is comparable to the angles of 93.14° in linear $CoCl_2(H_2O)_2$ and 93.10° in $CoCl_2$(4,4′- bipyridine).[6] The Co−Co distance between Co ions bridged by Cl^- is 3.570 Å, which is shorter than Co−Co distance in the linear chains in $CoCl_2$(bpy) (3.618 Å), $[(CH_3)_3NH]CoCl_3\cdot 3H_2O$ (3.637 Å), and the tetrameric compound $Co_4Cl_8(THF)_6$ (3.630−3.686 Å).[6] The Co−Co distance between Co ions connected by 1,4-dioxane is 7.137 Å. There are no weak interactions such as hydrogen bonds in the diamondoid framework of **2**.

In the CoO_4Cl_2 and CoO_2Cl_4 octahedra in **1** and **2**, respectively, the Co−O and Co−Cl distances fall into the ranges reported for octahedral compounds.[6] The crystal structures suggest that the transformation from **1** to **2** involves changes in the connecting mode of Cl^-, i.e., Cl^- acts as a μ-bridge in **2**, while the μ-bridges are interrupted by H_2O molecules in **1**.

On the basis of the extensive hydrogen bonds between chains in **1** and the three-dimensional diamondoid framework in **2**, long-range magnetic ordering could be expected in **1** and **2**.[1,7]

At 300 K, the χT value for **1** was 3.01 cm^3 K mol^{-1}, which is significantly larger than the value of 1.875 cm^3 K mol^{-1} expected for an isolated, spin-only ion with $S = {}^3/_2$ and $g = 2.00$ and close to a $Co^{2+}O_6$ octahedron, as a result of the significant orbital contribution of Co^{2+} ion due to strong spin−orbit coupling in an octahedral environment.[6h,i] The χT value decreased upon cooling and then increased rapidly below 4.4 K (Figure 2). The susceptibility data above 50 K fit the Curie−Weiss law well, giving Curie and Weiss constants of $C = 3.44(1)$ cm^3 K mol^{-1} and $\theta = -27.0(6)$ K, respectively, with $R = 9.31 \times 10^{-5}$. The negative Weiss value indicates antiferromagnetic interactions between Co^{2+} ions. The zero-field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) showed irreversibility below 3 K. The FCM of **1** was 146 cm^3 G mol^{-1} at ~2 K, and the remanent magnetization (RM) clearly indicated the spontaneous magnetization, reaching 13 cm^3 G mol^{-1} at ~2 K. This was further confirmed by ac measurements at 10, 100, and 1000 Hz, in which an increase in χ' and χ'' below 3.0 K and a very weak frequency dependence were observed (Figure 3). The isothermal magnetization was measured at 2 K. The magnetization increased quickly with increasing field, reaching 0.242 Nβ at 250 Oe, and then increased

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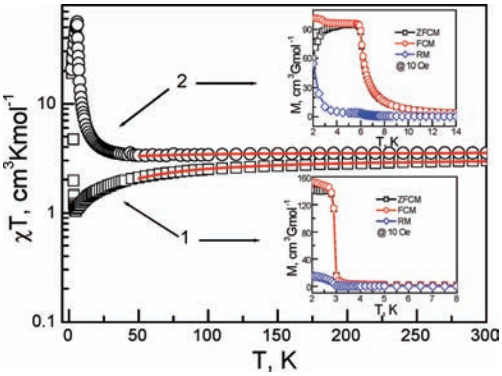

Figure 2. χT-vs-T plot for compounds **1** and **2** under an applied field of 100 Oe. Red solid lines are fits to the Curie−Weiss law. Insets: ZFCM/FCM/RM of (bottom) **1** and (top) **2** at 10 Oe.

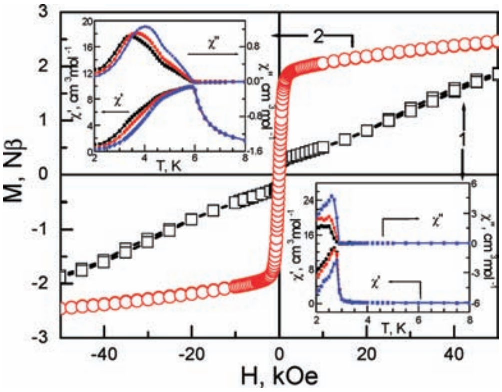

Figure 3. Isothermal magnetization plots for **1** and **2** at 2 K. Insets: Temperature dependence of ac susceptibility for (bottom right) **1** and (top left) **2** at an amplitude of 1 Oe and oscillation frequencies of (black) 10, (red) 100, and (blue) 1000 Hz in a zero-dc field.

slowly, reaching 1.86 Nβ at 50 kOe. This behavior may suggest the existence of weak ferromagnetism in **1**.[1f] The spin canting with a canting angle of 0.04° could be attributed to the local acentrosymmetry induced by hydrogen bonding, which is the requirement for the Dzyaloshinski−Moriya interaction.[8]

For **2**, at 300 K, the χT value was 3.52 cm^3 K mol^{-1}. The χT value decreased slowly upon cooling and then increased rapidly at 6.2 K (Figure 2). The susceptibility data above 50 K fit the Curie−Weiss law well, giving Curie and Weiss constants of $C = 3.56(1)$ cm^3 K mol^{-1} and $\theta = -3.9(3)$ K, respectively, with $R = 4.69 \times 10^{-5}$. The negative Weiss value indicates antiferromagnetic interactions between Co^{2+} ions. The ZFCM and FCM showed an irreversibility below 6 K. The FCM was 102 cm^3 G mol^{-1} at ~2 K, and the RM reached 54 cm^3 G mol^{-1} at ~2 K. The isothermal magnetization at 2 K displayed ferromagnetic behavior. The magnetization increased quickly, reaching 2.0 Nβ at 10 kOe, and then increased slowly, reaching 2.5 Nβ at 50 kOe. Saturation was not reached, but an extrapolated value of 3 Nβ at >100 kOe could be estimated.

It is well-known that the octahedrally coordinated Co^{2+} ion is most frequently Ising-like with $S_{\text{eff}} = {}^1/_2$ at low temperature. Thus, the 1D Ising chain model was applied to estimate the intrachain ferromagnetic coupling (J) and the deviation of the total weak effective interchain magnetic exchange (zJ') in the diamondoid framework of **2**.[9] The best-fit results from the susceptibility data between 12 and 40 K are $J = 17.4(4)$ cm^{-1}, $zJ' = -0.082(5)$ cm^{-1}, and $g = 5.01(3)$ with $R = 1.43 \times 10^{-6}$. The J value is larger than in other reported μ-Cl-bridged Co compounds,[6f] and the ferromagnetic coupling between μ-Cl-bridged Co^{2+} ions with Co−Cl−Co angles larger than 90° has been documented.[7] The difference between J and zJ' confirms the strong ferromagnetic interaction through (μ-Cl)$_2$ and the weak antiferromagentic interaction through 1,4-dioxane. The ferromagnetic ordering occurring at 6 K was further confirmed by ac measurements with an amplitude of 1 Oe and oscillation frequencies of 10, 100, 100 Hz in a zero-dc field (Figure 3, inset). The frequency-dependent behavior was observed from 2 to 8 K, The shift in the peak temperature of χ'' is in the range of that for spin glass.

The magnetic ordering temperature of **1** is lower than that of **2**, and the situation is totally different from that in the binary CoCl$_2$·xH$_2$O system, in which the ordering temperatures increase with the increasing H$_2$O content.[10] The anomaly may be ascribed to the Co−Co-distance-dependent magnetic interactions in **1** and **2**. Further experiments on single-chain magnets from the MCl$_2$(1,4-dioxane) system and detailed magnetic structures of **1** and **2** are in progress.

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Supporting Information Available: Sample preparation and characterization, Figures S1−S8, and X-ray crystallographic data for **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Wang, Z. M.; Zhang, B.; Fujiwara, H.; Kobayashi, H.; Kurmoo, M. *Chem. Commun.* **2004**, 416. (b) Kurmoo, M.; Kumagai, H.; Chapman, K. W.; Kepert, C. J. *Chem. Commun.* **2005**, 3012. (c) Armentano, D.; De Munno, G.; Mastropietro, T. F.; Julve, M.; Lloret, F. *J. Am. Chem. Soc.* **2005**, *127*, 10778. (d) Halder, G. J.; Kepert, C. J. *Aust. J. Chem* **2006**, *59*, 597. (e) Vittal, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1781. (f) Cheng, X. N.; Zhang, W. X.; Chen, X. M. *J. Am. Chem. Soc.* **2007**, *129*, 15738. (g) Cheng, X. N.; Zhang, W. X.; Lin, Y. Y.; Zheng, Y. Z.; Chen, X. M. *Adv. Mater.* **2007**, *19*, 1494. (h) Neville, S. M.; Halder, G. J.; Chapman, K. W.; Duriska, M. B.; Southon, P. D.; Cashion, J. D.; Létard, J.-F.; Moubaraki, B.; Murray, K. S.; Kepert, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 2869.

(2) (a) Maspoch, D.; Ruiz-Molina, D.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 190. (b) Zhu, W. H.; Wang, Z. M.; Gao, S. *Dalton Trans.* **2006**, 765. (c) Yoshida, Y.; Inoue, K.; Kurmoo, M. *Inorg. Chem.* **2009**, *48*, 267. (d) Ouellette, W.; Prosvirin, A. V.; Whitenack, K.; Dunbar, K. R.; Zubieta, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2140.

(3) (a) Boardman, A.; Small, R. W. H.; Worrall, I. J. *Acta Crystallogr.* **1983**, *C39*, 1005. (b) Barnes, J. C. *Acta Crystallogr.* **2004**, *E60*, m971.

(4) Barnes, J. C.; Weakley, T. J. R. *Acta Crystallogr.* **1977**, *B33*, 921.

(5) (a) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *Eur. J. Inorg. Chem.* **2003**, 1675. (b) Yu, J. H.; Lu, J.; Zhang, X.; Ye, L.; Hou, Q.; Xu, J. Q. *Inorg. Chem. Commun.* **2006**, *9*, 415.

(6) (a) Losee, D. B.; McElearney, J. N.; Shankle, G. E.; Carlin, R. L.; Cresswell, P. J.; Robinson, W. T. *Phys. Rev. B.* **1973**, *8*, 2185. (b) Greeney, R. E.; Landee, C. P.; Zhang, J. H.; Reiff, W. M. *Phys. Rev. B* **1989**, *39*, 12200. (c) Sobota, P.; Olejnik, Z.; Utko, J.; Lis, T. *Polyhedron* **1993**, *12*, 613. (d) Lawandy, M. A.; Huang, X. Y.; Wang, R. J.; Li, J.; Lu, J. Y.; Yuen, T.; Lin, C. L. *Inorg. Chem.* **1999**, *38*, 5410. (e) Hierso, J.-C.; Ellis, D. D.; Spek, A. L.; Bouwman, E.; Reedijk, J. *Chem. Commun.* **2000**, 1359. (f) Zhao, H.; Clerac, R.; Sun, J. S.; Ouyang, X.; Clemente-Juan, J. M.; Gomez-Garcia, C. J.; Coronado, E.; Dunbar, K. R. *J. Solid State Chem.* **2001**, *159*, 281. (g) Dan, M.; Rao, C. N. R. *Chem.—Eur. J.* **2005**, *11*, 7102. (h) Duan, Z. M.; Zhang, Y.; Zhang, B.; Zhu, D. B. *Inorg. Chem.* **2008**, *47*, 9152. (i) Duan, Z. M.; Zhang, Y.; Zhang, B.; Pratt, F. L. *Inorg. Chem.* **2009**, *48*, 2140.

(7) (a) Orendáčová, A.; Kajňoaková, M.; Černák, J.; Park, J.-H.; Čizmár, E.; Orendáč, M.; Vlček, A.; Kravchyna, O. V.; Anders, A. G.; Feher, A.; Meisel, M. W. *Chem. Phys.* **2005**, *309*, 115. (b) Desplanches, C.; Ruiz, E.; Alvarez, S. *Chem. Commun.* **2002**, 2614. (c) Ray, M. S.; Ghosh, A.; Bhattacharya, R.; Mukhopadhyay, G.; Drew, M. G. B.; Ribas, J. *Dalton Trans.* **2004**, 252. (d) Paine, T. K.; Weyhermuller, T.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **2002**, *41*, 6538.

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

(9) (a) Fisher, M. E. *J. Math. Phys.* **1963**, *4*, 124. (b) Sato, M.; Kon, H.; Akoh, H.; Tasaki, A.; Kabuto, C.; Silverton, J. V. *Chem. Phys.* **1976**, *16*, 405. (c) Liu, T.; Zhang, Y. J.; Wang, Z. M.; Gao, S. *Inorg. Chem.* **2006**, *45*, 2782.

(10) Carlin, R. L. *Magnetochemistry*; Springer: Berlin, 1986; p 119.

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