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Reversible Single-Crystal-to-Single-Crystal Transformation from Achiral Antiferromagnetic Hexanuclears to a Chiral Ferrimagnetic Double Zigzag Chain

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Tunable molecular magnets, whose structures and properties are sensitive to external stimuli such as light, heat, pressure, and guest molecules, are attracting increasing interest for their potential applications as switches and sensors.[1] One of the most appealing is the modification of spin topology through cooperative solid state transformations, especially those producing reversibility. But it is still a challenge, especially for those transformations involving the breaking/forming of the coordination bonds. Only limited single-crystal-to-single-crystal (SCSC) transformations involving the dimensionality changes of coordination complexes have been reported. Few of these transformation have been documented to generate a tunable magnetic system.[2] Here, we report a reversible SCSC transformation from achiral hexanuclear clusters to a chiral one-dimensional (1D) double-zigzag chain via generation/cleavage of coordination bonds. The interconversion between a monomer and coordination polymer involves the reversible change in magnetization between antiferromagnetic in a zero-dimensional (0D) cluster and ferrimagnetic in a 1D chain.

A solid state reaction proceeds under the condition in which crystal packing and molecular orientation are suitable for a topochemical reaction.[3] Such an orientation can be controlled using directional supermolecular interactions such as hydrogen bonding and $\pi-\pi$ stacking.[4] To induce the reversible crystalline phase reaction, we focused on the hexanuclear cluster $[\{Fe^{III}(Tp)(CN)_3\}_4\{Fe^{II}(MeCN)(H_2O)_2\}_2]\cdot 10H_2O\cdot 2MeCN$ (**1**) (Tp = hydrotris(pyrazoly)borate). **1** crystallizes in the $P2_1/c$ space group. The structure of **1** (Figure 1a) is isomorphous with that reported for $Fe^{III}_4M^{II}_2$ [M = Ni, Co, Mn],[5] containing neutral hexanuclear clusters with uncoordinated solvent molecules between them. In the hexanuclear unit, two bidentate $[Fe(Tp)(CN)_3]^-$ anions link two Fe^{II} ions through CN^- bridges, forming an $[Fe^{III}_2Fe^{II}_2(CN)_4]^{6+}$ square unit. The other two $[Fe(Tp)(CN)_3]^-$ anions are monodentate and bond to two Fe^{II} ions with *cis*−*trans* geometry with respect to the bridging $[Fe(Tp)(CN)_3]^-$ anion. Each Fe^{II} is further coordinated with one acetonitrile and two water molecules. The $Fe^{II}-N-C$ angles are 154.4°−172.0°. The intramolecular $Fe^{III}\cdots Fe^{II}$ distances are 5.089−5.189 Å, and the shortest intermolecular $Fe\cdots Fe$ distance is 7.589 Å.

An important characteristic of **1** is that the hexanuclear units are linked to each other to form a chain through hydrogen bonding interactions of the terminal CN^- on the $[Fe(Tp)(CN)_3]^-$ moiety and the weakly coordinated solvent molecules on Fe^{II} on two diagonal sides of the square core $Fe^{III}_2Fe^{II}_2$. Hence, it is expected that the solvent molecules are removed on heating, and concomitantly, CN^- coordinates to the free sites of Fe^{II} of a neighboring cluster, allowing a solid state reaction that forms a one-dimensional polymer structure. We performed thermogravimetric analysis (TGA) (Figure S1) and powder X-ray diffraction (XRD) (Figure S2) measurements to verify the solid state reaction. The TGA of **1** displays a weight loss of 20.7% from 40 to 90 °C, corresponding to the loss of 12 water molecules and 4 acetonitrile molecules (19.9%). After the weight loss, a long plateau is observed up to the point where decomposition occurs at *ca.* 250 °C, suggesting the formation of a new phase of $[Fe^{III}(Tp)(CN)_3]_4Fe^{II}(H_2O)_2Fe^{II}$ (**2**), as shown by the powder XRD patterns.

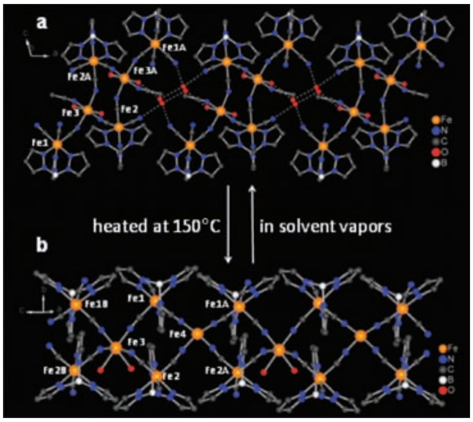

Figure 1. (a) Side view of the chain formed by hexanuclear units and $(H_2O)_4$ ring through hydrogen bonds in **1**. (b) Side view of the 1D double zigzag chain in **2**. H atoms are omitted for clarity.

Single crystals of **2** were obtained by slowly heating crystals of **1** to 150 °C under an N_2 atmosphere. Single-crystal XRD revealed that **2** crystallizes in the $C2$ space group with Flack parameters near zero, suggesting that **2** has a chiral structure; i.e., the transformation accompanies the change in chirality from achiral **1** to chiral **2**. Within the chain (Figure 1b), each $[Fe(Tp)(CN)_3]^-$ entity acts as a bidentate ligand toward two Fe^{II} ions through two of its three cyanide groups in *cis* positions, affording bimetallic double chains that run parallel to the *c* axis. These double chains show two orientations of their mean planes ($Fe^{III}_2Fe^{II}_2$), with a dihedral angle of 84°. The polymer **2** consists of two types of Fe^{II} ions: octahedrally coordinated Fe3 and tetrahedrally coordinated Fe4, alternating along the chain. Each Fe^{II} is coordinated to four nitrogen atoms via CN^- bridges, and the two remaining sites in the *cis* position of the octahedral Fe^{II} are occupied by two water molecules. Structural rearrangement should occur in solid state reactions, because two water molecules occupy two sites in the *trans* positions of Fe^{II} in **1**. Except for the capping tridentate *fac*-Tp anion, the linkages of the three CN^- of the Fe^{III} are different. One is terminal, another bridges one octahedrally coordinated Fe^{II}, and the third bridges one tetrahedral Fe^{II}. This arrangement forces Fe^{III} to be the chiral center. Moreover, the chain lacks a center of symmetry and symmetry plane due to the *cis* arrangement of two water molecules of octahedrally coordinated Fe3 and the distorted tetrahedral con-

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figuration of Fe4, ensuring the chirality of **2**. The $Fe^{II}-N-C$ angles range from 152.3° to 177.3°. The intrachain Fe···Fe distances are 5.164−5.178 Å, and the shortest interchain Fe···Fe distance is 7.877 Å. It is worth mentioning that chains with the structure of **2** have never been obtained by reactions in solution. In fact, for the achiral chain formed by $[Fe(Tp)(CN)_3]^-$, and other M^{II} ions through solution reactions, the M^{II} ions are uniformly and octahedrally coordinated, and two coordinated solvent molecules occupy the *trans* position of the M^{II} ions.[6] This confirms that solid state reactions can provide access to molecules otherwise difficult or impossible to obtain from reactions in solution.

The transformation from **1** to **2** involves changes in the symmetry, lattice parameters, and molecular stacking arrangements (Figure S3). When placed in a vapor of mixed water and acetonitrile, the reversible transformation from **2** to **1** occurred, as evidenced by powder XRD patterns (Figure S2). To the best of our knowledge, this is the first example of a reversible SCSC polymerization from achiral 0D to a chiral 1D coordination complex.

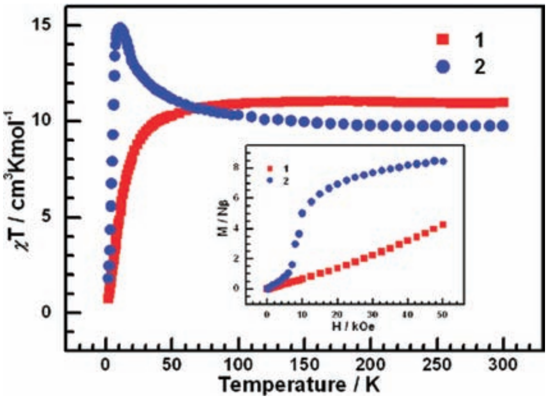

Figure 2. χT vs T plots under a 1 kOe field and M vs H plots at 2 K (inset) for **1** and **2**.

As the structure changes drastically, significant changes in magnetic properties are to be expected. At room temperature, the χT values (Figure 2) of **1** are 10.95 cm^3 K mol^{-1} per $Fe^{III}{}_4Fe^{II}{}_2$, being larger than the spin-only value for four Fe^{III} with $S = {}^1/_2$ and two Fe^{II} with $S = 2$, due to the orbital contribution of Fe^{III} and Fe^{II}. The magnetic susceptibility data above 30 K fit the Curie−Weiss law well, providing a Curie constant of 11.12 cm^3 K mol^{-1} and Weiss temperature of −2.95 K, indicating the dominant weak antiferromagnetic interactions within the material. On cooling, the χT values decrease more and more rapidly, finally reaching a small value, 0.76 cm^3 K mol^{-1}, at 2.0 K. The maximum of χ is observed at 10.0 K (Figure S4). Neither the real component nor the imaginary component of *ac* susceptibility shows a maximum (Figure S5), indicating no long-range antiferromagnetic ordering, and hence short-range interactions. The field-dependent magnetizations, even at 2 K and 50 kOe, being 4.29 Nβ, far from the saturated values of 12.0 Nβ for $g = 2.0$, confirm the significant antiferromagnetic interactions in **1** (Figure 2 insert). According to the proposed structure, the intrahexanuclear interactions should be strong, and the interhexanuclear interactions should be weak. Hence, the hexanuclear unit should be intrinsically antiferromagnetic.

For **2**, the χT values at room temperature are 9.75 cm^3 K mol^{-1} per $Fe^{III}{}_4Fe^{II}{}_2$, smaller than that in **1** due to the different orbital contribution between tetrahedral Fe^{II} and octahedral Fe^{II}. On cooling, the χT values increase more and more quickly, reaching a very sharp maximum of 14.9 cm^3 K mol^{-1} at 11.0 K (Figure 2) and then quickly decrease to low values of 1.79 cm^3 K mol^{-1} at 2.0 K. The high temperature data fit the Curie−Weiss law well and provide Curie and Weiss constants $C = 9.46$ cm^3 K mol^{-1} and $\theta = 7.43$ K, suggesting dominant ferromagnetic interaction in **2**. Further magnetic investigation reveals that **2** is a metamagnet. Upon increasing field strength, the maxima in its magnetizations moved to lower temperatures and became less prominent and finally disappeared at 9.0 kOe for **2**, indicating a metamagnetic transition induced by the external field (Figure S6). The Neel temperature T_N determined by the peak of the real component of *ac* susceptibility is 7.0 K, and no peak was found for the imaginary component (Figure S7). The field-dependent magnetizations, 8.50 Nβ per $Fe^{III}{}_4Fe^{II}{}_2$ at 2 K and 50 kOe, suggest a ferrimagnetic ground state with $S = 4$ for $g = 2.125$ (Figure 2 insert). The sigmoidal shape of the field-dependent magnetizations at 2 K exhibits a field-induced transition from an antiferromagnetic to a ferrimagnetic state. Below 4 kOe, the magnetizations are small, whereas from 5.0 to 12.0 kOe they increase quickly. Above 12.0 kOe, the increase in magnetization slows, and its dependence on field strength is nearly linear. Given the proposed structure, strong intrachain interactions and weak interchain interactions are expected. It is reasonable to say that the intrachain interactions are ferrimagnetic, and antiferromagnetic interactions come from the weak interchain interactions. The crossover between an antiferromagnetic hexanuclear cluster and a ferrimagnetic double zigzag chain may be caused by the variation of the $Fe^{II}-N-C$ angle and accidental orthogonality (see Supporting Information).[6,7]

In summary, a reversible SCSC transformation from an achiral antiferromagnetic hexanuclear cluster to a chiral ferrimagnetic double zigzag chain has been established. Our approach should result in the creation of a complete family of SCSC transformation complexes, involving switchable chirality and magnetic interactions, and a novel method for preparing chiral magnets.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1** and **2**, a PDF file containing further information about synthesis, magnetic properties, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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