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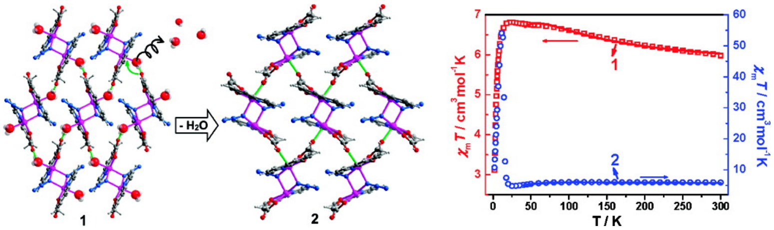

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Single Crystal-to-Single Crystal Transformation from Ferromagnetic Discrete Molecules to a Spin-Canting Antiferromagnetic Layer

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Molecular magnets whose properties are sensitive to the external stimulus, are recently very attractive for their potential applications as switches and sensors.[1] The weak interaction of guest molecules, coordination geometry distortion, and coordination number change can effectively modulate the magnetic properties of coordination polymers.[2] Obviously, modification of the spin exchange topology, for example, connecting discrete magnetic clusters into an extended network, is expected to induce more drastic magnetism change.[3] However, the poor crystallinity of the final product often prevents the structural determination after solid-state transformations, especially those involving the breakage/formation of chemical bonds.[4] So far only limited single crystal-to-single crystal (SCSC) transformations involving the dimensionality changes of coordination polymers were reported,[5] and no such transformation has been utilized in generating a dynamic magnetic system. Here, we report a SCSC transformation from discrete molecules into two-dimensional (2D) layers, concomitant with a drastic change in magnetic properties.

Quinoline-8-oxy-acetate (8-qoac), as a multidentate ligand with a carboxylate group, was designed to generate both discrete complex and extended magnetic networks. The 0D dimeric compound $[Co_2(8\text{-qoac})_2(N_3)_2(H_2O)_2]$ (**1**) was synthesized by the reaction of 8-Hqoac, $Co(NO_3)_2$, and NaN_3 in CH_3OH/H_2O. The single-crystal structure of **1**[6] consists of double end-on (EO) azido-bridged, centrosymmetric Co^{II} dimers (Supporting Information, Figure S1). The Co^{II} ion is ligated by a tridentate 8-qoac, two azido, and one aqua ligand in a highly distorted octahedral N_3O_3 geometry (Co−N/O, 2.034−2.176 Å). In the resulting planar Co_2N_2 ring, the Co−N−Co angle (99.22(9)°) and the Co⋯Co distance (3.226 Å) lie in the typical range for double EO azido-bridged structures.

An interesting feature in **1** is that the supramolecular interactions may direct a solid-state reaction. Each aqua ligand is hydrogen-bonded to an uncoordinated carboxy oxygen atom of an adjacent dimer [O−H⋯O 2.660(1) Å], resulting in a hydrogen-bonded, wavy (4,4) network (Figure 1), which stacks via $\pi-\pi$ interactions into a 3D architecture (Figure S2). When the aqua ligands are removed, the uncoordinated carboxy oxygen atom may take up the vacant site of Co^{II} in a neighboring dimer, forming a mixed azido/carboxylato-bridged layer. Thermogravimetric analysis (TGA) of **1** displays a weight loss of 5.7% from 165 to 190 °C, corresponding to the loss of the aqua ligands (5.6%) (Figure S3). After this weight loss, a long plateau is observed until a full decomposition at ca. 270 °C occurs, where a new phase is formed upon removing the aqua ligands in the range of ca. 150−190 °C, as shown by temperature-dependent powder X-ray diffraction patterns (PXRD) (Figure S4). Fortunately, we were able to obtain, though irreversibly, the dehydrated single crystals $[Co_2(8\text{-qoac})_2(N_3)_2]_n$ (**2**) by heating the single crystals of **1** at 150 °C under vacuum.

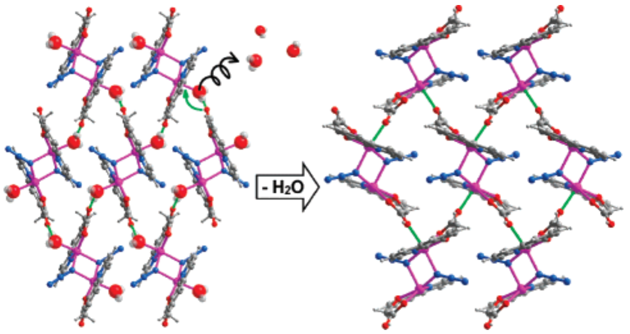

Figure 1. Transformation of the 0D dimer **1** (left) to the 2D layer structure in **2** (right). (The water molecules in **1** are highlighted by enlargement; the black and green arrows represent the removal of an aqua ligand and the possible attacking of an uncoordinated carboxy O atom to the Co^{II} atom of an adjacent dimer, respectively.)

Crystallography study revealed that the dimeric unit in **2**[6] resembles that of **1** (Co−N/O 2.014−2.197 Å, Co⋯Co 3.232 Å, Co−N−Co 100.5(1)°). However, the aqua ligand is now replaced by a carboxy oxygen atom from a neighboring dimeric unit, thus each dimer is now connected to four neighboring ones by the anti−anti carboxylate bridges, giving rise to a (4,4) layer by considering each dimer as a node. The coordination structure in **2** may also be described as anti−anti carboxylato-bridged Co^{II} helical chains interlinked by the double EO azido bridges. The helicity leads to two different orientations of metal coordination spheres alternating along the helix, which is an important implication for the spin-canting magnetic behavior.[7]

The crystal structures imply that the transformation from **1** to **2** involves changes in the symmetry, lattice parameters,[6] dimer orientations (Figure 1), and molecular stacking fashions (Figure S2). It is also notable that this transformation is the first example of a SCSC transformation from 0D metal complexes to a 2D coordination polymer, though a 0D to 2D solid-state structural transformation of an inorganic anion $[H_2V_{10}O_{28}]^{4-}$ was previously established by TGA and PXRD techniques.[5c]

Magnetic properties for polycrystalline **1** and **2** were measured. The $\chi_M T$ value per dimer of **1** is 5.97 cm^3 mol^{-1} K at 300 K, which is typical for an octahedral Co^{II} complex. The $\chi_M T$ versus T plot of **1** at 1000 Oe (Figure 2) increases first upon cooling for an intradimer ferromagnetic coupling (the Weiss constant $\Theta = 14.2$ K, fitting from 80 to 300 K), then rapidly decreases to 2 K, owing to weak interdimer antiferromagnetic interaction and/or zero-field splitting effects. This behavior is consistent with the other double EO azido-bridged dimers.[7c] To roughly estimate the magnetic interaction between Co^{II} ions, a spin-only dimeric model of Co^{II}, with J as the intradimer interaction and θ as a correction item including the interdimer interaction and orbital contribution, is used (see ESI). The least-squares fit of the experimental data above 40 K of **1** leads to $J = 10.4$ cm^{-1}, $\theta = -11.3$ K, $g = 2.44$, $R = 2.1 \times 10^{-5}$. The positive J value shows the strong intradimer ferromagnetic coupling, consistent with the typical double EO azido-bridged dimers.[7] The negative θ accounts for the orbital contribution

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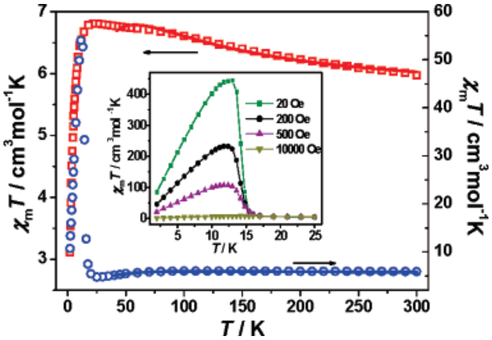

Figure 2. The temperature-dependent susceptibility of **1** (red) and **2** (blue). The solid lines are the best fit to the spin-only dimer Co^{II} model for **1** and **2**. Inset: FC magnetizations at different fields for **2**.

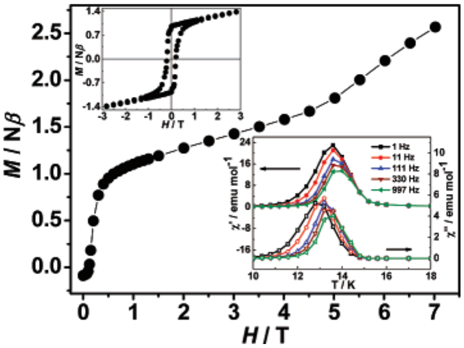

Figure 3. The isothermal magnetization for **2** at 2 K. The insets show the temperature dependence of *ac* susceptibility at various frequencies for **2** (lower right) and the hysteresis loop for **2** at 2 K (upper left).

of Co^{II} ion and interdimer antiferromagnetic interaction (see ESI). The ferromagnetic interaction is also confirmed by the isothermal magnetization at 2 K, which increases rapidly and saturates with the field up to 7 T. Moreover, neither peak of long-range magnetic ordering in *ac* susceptibility data nor hysteresis loop is observed for **1** (Figures S5 and S6).

The magnetic behaviors of **2** are distinctly different from those of **1** owing to the presence of the antiferromagnetic anti−anti carboxylate bridges. The $\chi_M T$ of **2** is almost invariable down to 60 K (with $\Theta = 2.9$ K), and then slowly decreases to a minimum at ca. 25 K (Figure 2). This behavior should be attributed to the competition of the spin−orbit coupling, intradimer ferromagnetic, and interdimer antiferromagnetic interactions of Co^{II}. Below 25 K, the $\chi_M T$ value rises abruptly to a sharp maximum at ca. 11 K, and finally drops rapidly to 2 K for the interlayer antiferromagnetic interaction and/or zero-field splitting effects. The sharp increase of $\chi_M T$ value suggests that the local spins adopt a spin-canting configuration being consistent with the structure of **2**. Although the double EO azido-bridged dimer is centrosymmetric, there is no inversion center within the anti−anti carboxylato-bridged Co^{II} helical chain. Thus, spin canting can occur throughout the chain.[7] As expected for a weak ferromagnet due to spin canting, the magnetic behavior of **2** is markedly field-dependent (Figure 2 inset). To compare the magnetic interactions roughly yet directly with those in **1**, the experimental data of **2** above 40 K are fitted by the same model for **1**, leading to $J = 13.8$ cm^{-1}, $\theta = -27.0$ K, $g = 2.41$, $R = 3.1 \times 10^{-6}$. The J value is comparative with that of **1**, while the much larger $|\theta|$ than that of **1** may be attributed to the presence of anti−anti carboxylate bridges, which significantly enhance the interdimer antiferromagnetic interaction of **2**.

To further characterize the weak ferromagnetism in **2**, the isothermal magnetization and the hysteresis loop were measured at 2 K. The magnetization first increases slowly in the low field for the interlayer antiferromagnetic interaction (Figure 3), and then increases abruptly at 750 Oe for the intradimer ferromagnetic interactions. Upon a further increase of the field, the magnetization increases much more slowly as the ferromagnetic phase tends to saturate. Finally, the magnetization increases linearly for the higher fields, which is a feature of spin-canting antiferromagnet. The M value at 7 T is 2.57 Nβ, which is far below that expected for a total alignment of spins ($M \approx 6$ Nβ) for the canting antiferromagnetic interactions in **2**. A hysteresis loop of **2** is observed at 2 K with a remnant magnetization 1.0 Nβ and a coercive field of 1980 Oe per dimer (Figure 3 inset). The obvious frequency-dependent behavior was observed in the *ac* susceptibility data from 11 to 15 K (Figure 3 inset). The shift of peak temperature (T_p) of χ'' was measured by a parameter $\phi = \Delta T_p/[T_p\Delta(\log f)] = 0.01$, being in the range of spin glass. This behavior confirms the presence of the long-range order in **2**. The critical temperature 13 K of the phase change is attested by ZFC and FC curves (Figure S7).

In summary, a unique SCSC transformation from 0D discrete molecules to a 2D coordination polymer has been established, which is accompanied by the drastic magnetic property change from short-range coupling to long-range spin-canting antiferromagnetic ordering.

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Supporting Information Available: Synthesis; crystal data in CIF files; IR, PXRD, and additional magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Crystal data. **1**: 293(2) K, monoclinic $P2_1/n$, $a = 8.0040(6)$ Å, $b = 17.281(1)$ Å, $c = 9.5685(8)$ Å, $\beta = 111.599(1)^o$, $V = 1230.6(2)$ Å^3, $Z = 2$, $D_c = 1.734$ g cm^{-3}, final $R_1 = 0.0394$ ($I \geq 2\sigma$), $wR_2 = 0.0950$ (all data), $S = 1.113$. **2**: 293(2) K, monoclinic $P2_1/c$, $a = 9.722(3)$ Å, $b = 7.723(2)$ Å, $c = 15.010(4)$ Å, $\beta = 91.352(5)^o$, $V = 1126.7(6)$ Å^3, $Z = 4$, $D_c = 1.787$ g cm^{-3}, final $R_1 = 0.0457$ ($I \geq 2\sigma$), $wR_2 = 0.1020$ (all data), $S = 1.108$.

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