Low-Dimensional Magnet

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Assembling Magnetic Nanowires into Networks: A Layered Co^{II} Carboxylate Coordination Polymer Exhibiting Single-Chain-Magnet Behavior**

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Chemists and physicists have jointly pushed the rapid progress of molecule-based nanomagnets in recent years.[1] Since the first discovery of single-molecule magnets (SMMs) in the 1990s,[2] exciting discoveries in this area have included single-chain magnets (SCMs, or so-called magnetic nanowires)[3] and a hydrogen-bonded SMM dimer,[4] which can be regarded as expansions of SMMs by intermolecular magnetic interactions.[4,5] These observations have encouraged chemists to construct or tailor SMMs into an extended network with the hope that certain cooperative effects mediated by covalent linkers could improve the quantum properties of the original units.[5–7] This idea has led to a variety of interesting SMM networks exhibiting properties from classical to quantum magnetism[6,7] and provided useful subjects for studying the effects of intermolecular interactions on the behavior arising from the energy barrier to magnetization reversal.[4–7] In contrast to the rapid development of SMM networks, SCM networks are significantly restricted, which may be attributable to the difficulty in arranging these magnetic nanowires while maintaining a sufficiently large ratio of intra- to interchain magnetic interaction to "freeze in" one-dimensional (1D) magnetization and prevent 3D ordering.[3] Thus, it is important to use proper covalent linkers, which should have at least two features: 1) multitopic structure to covalently link the chains; 2) magnetically "inertness" to efficiently prevent magnetic interactions between the chains.

As σ-bonding linkers are significantly weaker mediators of the spin carriers,[8] crystal engineering with a judicious choice of σ-bonding ditopic linkers may allow us to covalently link 1D Ising ferro- or ferrimagnetic chains into 2D or 3D networks without significant deterioration of the one-dimensional magnetism of the SCMs in the 2D or 3D structures, although no genuine example has been reported so far. In this regard, *trans*-1,2-cyclohexanedicarboxylate (*trans*-1,2-chdc) is a good candidate, since it was demonstrated to be a very weak magnetic mediator[9] due to alternation effects.[8]

As part of our ongoing search for new magnetic coordination polymers,[10] we chose this ligand as a structural linker and magnetic separator to incorporate magnetic anisotropic chains into a higher dimensional network. We have used *trans*-1,2-chdc to prepare laminated coordination polymer $^{2}_{\infty}[Co^{II}_{3}(OH)_2(trans\text{-}1,2\text{-}chdc)_2]$ (**1**) exhibiting magnetism due to coexistent spin frustration and long-range magnetic ordering.[10a] Interestingly, at lower reaction pH value and temperature, we obtained the new laminated product $^{2}_{\infty}[Co^{II}(trans\text{-}1,2\text{-}chdc)]$ (**2**) as a pure phase, which consists of a parallel arrangement of carboxylate-bridged, paddle-wheel Co^{II} chains and shows interesting SCM behavior.

In the single-crystal structure of **2**, the Co^{II} atom (Figure 1 and Figure S1) adopts a slightly distorted square-pyramidal geometry with four basal oxygen atoms (Co–O 1.971(3)–2.210(3) Å) and one apical oxygen atom (Co–O 2.019(3) Å) giving a small τ value of 0.028 ($\tau = 0$ for an ideal square pyramid)[11] and slight displacement (0.34 Å) of the Co^{II} atom from the basal plane. A pair of inversely related Co^{II} ions are bridged by four μ-carboxylate groups into a paddle-wheel dimer with an intradimer $Co^{II}\cdots Co^{II}$ distance of 2.912(1) Å. Interestingly, a pair of such adjacent, inversely related Co^{II} dimers are bridged by a pair of μ-carboxylato-O bridges (Co-O-Co 101.1(1)°; interdimer $Co^{II}\cdots Co^{II}$ distance 3.269(1) Å) to form a chain that is structurally analogous to those observed previously for Cu^{II}, Rh^{II}, and Ni^{II}.[12] Adjacent chains are interlinked into layers by *trans*-1,2-chdc ligands with a shortest interchain $Co^{II}\cdots Co^{II}$ distance of about 5.5 Å. Such

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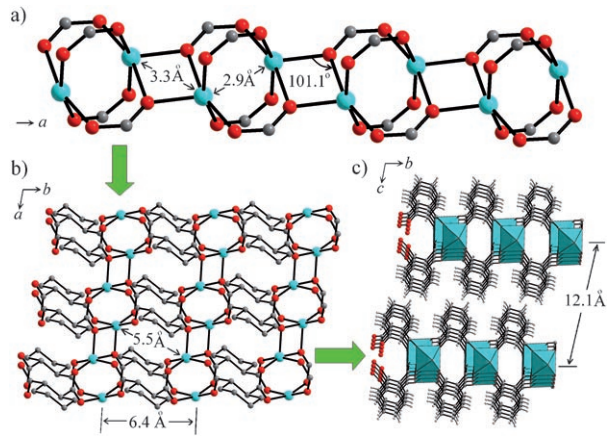

Figure 1. Perspective views of the a) paddle-wheel chain, b) layer, and c) crystal packing with the Co^{II} atoms highlighted as blue polyhedra in **2** (C gray, Co blue, O red).

layers are further stacked along the *c* axis solely by van der Waals interactions with a shortest interlayer $Co^{II}\cdots Co^{II}$ distance of about 12.1 Å.

The effect of this structural arrangement on the magnetism of **2** is evident. The dc susceptibility data (Figure 2) measured on a powder sample of **2** show that the χT value of **2**

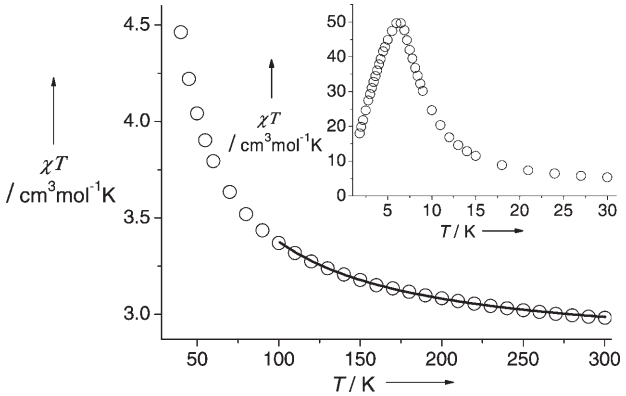

Figure 2. Plot of χT vs. *T* at an applied field of 500 Oe from 50 to 300 K; solid line: fitted by the modified Fisher model for 1D alternating chain ($S=^3/_2$). Inset: χT vs. *T* plot from 2 to 30 K.

at 300 K is 2.98 $cm^3 mol^{-1} K$ per Co^{II} ion, which is significantly larger than the spin-only value of 1.88 $cm^3 mol^{-1} K$ and hence indicates a large orbital contribution. On cooling, it gradually increases to about 30 K without the presence of a minimum, and the data in the range of 50–300 K obeys the Curie–Weiss law ($\chi_m = C/(T-\theta)$, with $C = 2.83\ cm^3 mol^{-1} K$ and $\theta = 15.87$ K). The set of data above 100 K were well fitted by the modified Fisher model for a 1D alternating chain ($S=^3/_2$), and the spin Hamiltonian[13] reads as Equation (1), where J_1 and J_2 are the intrachain alternating coupling constants, and the interchain interactions are described by the mean-field approximation: $\chi_M = \chi_{chain}/(1-zJ'\chi_{chain}/Ng^2\beta^2)$; for magneto-structural correlation, see Scheme S1. The best fit gave $J_1/k_B = 11.51$ K, $J_2/k_B = 3.95$ K, $g = 2.45$, $zJ'/k_B = -0.01$ K, and $R = 4.5\times10^{-5}$, where $R = S[(\chi_{mT})_{obs}-(\chi_{mT})_{calcd}]^2/[(\chi_{mT})_{obs}]^2$.[13]

$$H = -J_1 \sum S_{2i}\, S_{2i+1} - J_2 \sum S_{2i+1}\, S_{2i+2} \qquad (1)$$

The two positive values ($J_1 > J_2 > 0$) reveal that the intrachain interactions are ferromagnetic and inequivalent. Assuming the fitting results are correct, the ratio $|J'/J_{average}|$ (assuming $z=2$) of about 6.5×10^{-4} indicates that the magnetic interchain interactions are very weak compared with the intrachain interaction.[3a] The undoubtedly ferromagnetic coupling within the tetracarboxylate-bridged Co^{II} paddle wheels is unprecedented.[14] The data below 30 K (inset of Figure 2), however, show a not-so-round peak at 6.0 K (usually, a round peak correlates with 1D behavior, while a cusp suggests 3D ordering).[3j] Similar peaks were also observed in some previously reported SCMs[3b,f,k] and were explained as a short-range saturation effect[3f] or 1D Ising behavior.[3b] Since the magnetic field applied to **2** was only 500 Oe, this not-so-round peak is more likely to correlate with Ising-like ferromagnetic behavior rather than the saturation effect or a 3D ordered phase,[15] and this required further study.

Therefore, we performed magnetization measurements on an orientated single crystal of **2** in order to understand the low-temperature magnetism of **2** in more detail. As shown in Figure 3, the magnetization is significantly anisotropic below 50 K. Rotational measurements of magnetization on a single crystal of **2** (Figure S2) reveal an unambiguously uniaxial anisotropic magnetism.[16] The uniaxial anisotropic behavior is also reflected in the field dependence of magnetization along the easy-axis direction (inset of Figure 3), which quickly saturates at $4.10\mu_B$ per Co^{II} unit.

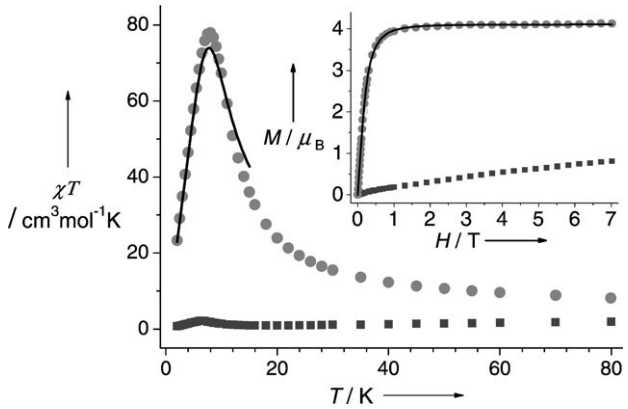

Figure 3. Field-cooled magnetization with an applied field of 2 KOe from 80 to 2 K of a single crystal of **2** along (●) and perpendicular to the easy-axis direction (■); solid line: best fit of the 1D Ising model. Inset: Field dependence of the magnetization at 10 K; solid line: best fit of the 1D Ising model.

To model these results, the simplest relevant approach is 1D Ising model with $S=^1/_2$ and anisotropic *g* value, since the Co^{II} ion is most frequently Ising-like with $S_{eff}=^1/_2$ at low temperatures (typically below 30 K),[16] the Hamiltonian

can be written as Equation (2). To identify this expression with Glauber's notation,[17] one should introduce $\sigma_i = -2S_{Tz,i}$ ($=\pm 1$), and the Hamiltonian now is expressed by Equation (3).[3b,18]

$$H = -J_{eff}\sum S_{Tz,i}S_{Tz,i+1} + g_z\mu_B H_z \sum S_{Tz,i}\ ;\ J_{eff} = J_1 = J_2 \qquad (2)$$

$$H = -J'_{eff}\sum \sigma_i\sigma_{i,i+1} - \mu_{eff}H\sum \sigma_i\ ;\ J'_{eff} = {}^1\!/_4 J_{eff}\ ,\ \mu_{eff} = {}^1\!/_2 g_z\mu_B \qquad (3)$$

This model gives the magnetization as the function of temperature and magnetic field [Equation (4)].[3b,18]

$$M = N\mu_{eff}\sin h(\mu_{eff}H/k_B T)/[\sin h^2(\mu_{eff}H/k_B T) + \exp(-4J'_{eff}/k_B T)]^{1/2} \qquad (4)$$

This expression was used to fit the data between 2 and 15 K (solid lines in Figure 3 and its inset), and this led to $g_z = 8.20$, $\mu_{eff}/\mu_B = {}^1\!/_2 g_z = 4.10$, $J'_{eff}/k_B = 8.89$ K, and $R = 8\times10^{-4}$. This satisfactory result confirms that the χT peak and the rapid saturation of the magnetization along the chain (inset of Figure 3) is compatible with 1D Ising behavior and does not imply long-range ordering.

Below 3.5 K, irreversibility effects are observed in static magnetic measurements as the discrepancy between zero-field-cooled (ZFC) and field-cooled (FC) magnetization in an applied external field (Figure S3). Furthermore, hysteresis loops clearly appear below 2.2 K with orientation- and temperature-dependent shape (Figure 4). Along the easy-axis direction, the coercive fields are 5, 31, and 165 Oe at 2.2, 2.0, and 1.8 K, respectively. Interestingly, the coercive field and the saturated magnetic moment along the easy-axis direction at 1.8 K are almost twice that of the powder sample (Figure S4). It is also noteworthy that the hysteresis loops along the easy-axis direction exhibit "steps" at the original region due to the effect of weak interchain interaction,[3j] which can be easily overcome by a small external field. The dM/dH curve at 1.8 K clearly shows that the critical field H_C is 45 Oe in this direction, which could be used to estimate the interchain interaction by the expression $g_z\mu_B H_C S_T = 2|zJ'|S_T^2$,[19] giving $|zJ'| = 0.025$ K ($S_T = {}^1\!/_2$). This result is in agreement with the $|zJ'|$ value obtained from the alternating chain model with $S = {}^3\!/_2$ and provides further support for the weak interchain interaction. Even though such aforementioned behaviors are usually observed in ferro-/ferrimagnetically ordered magnetism, another possibility could be the presence of a frozen magnetized state caused by the strong anisotropy.[3b] To gain more insight into the magnetic properties of **2**, we performed detailed ac magnetic measurements.[20]

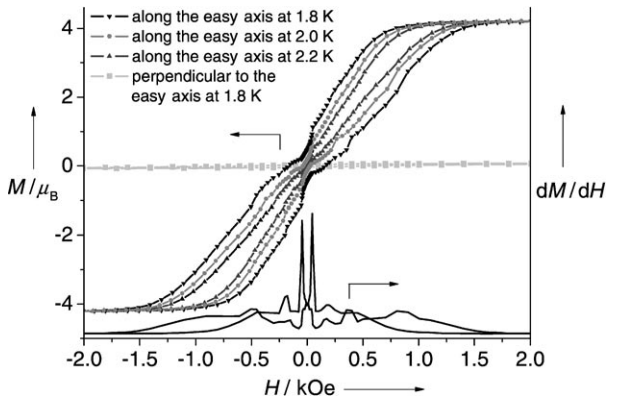

Figure 4. Top: hysteresis loops of a single crystal of **2**. Bottom: Plot of dM/dH vs. H at 1.8 K.

Below 6.5 K, the real (χ') and imaginary (χ'') components of the ac susceptibility are strongly frequency-dependent (Figure 5). This behavior precludes any significant 3D ordering, and confirms that the very "robust" Glauber dynamic region is unaffected by possible weak interchain interactions.[3j,21] The peak temperatures T_p of χ'' can be well fitted by the Arrhenius plot extracted from these data (inset of Figure 5, bottom), which shows the occurrence of a clear crossover between two different activated regions at $T^* = 4.4$ K ($1/T^* = 0.227$ K^{-1}), giving best-fit physical τ_0 values of 5.19×10^{-11} and 5.59×10^{-8} s for the high- and low-temperature regions, respectively, and two corresponding different barriers ($\Delta_{\tau1}/k_B = 80.9$ and $\Delta_{\tau2}/k_B = 50.2$ K). This result is in agreement with the observed finite-size effect (i.e., the presence of structural defects on the chain which limit the growth of the correlation)[22] halving the Glauber activation barrier for SCMs. This crossover behavior is also evident from the plot of ln(χT) versus 1/T. Figure S5 shows ln(χT) increas-

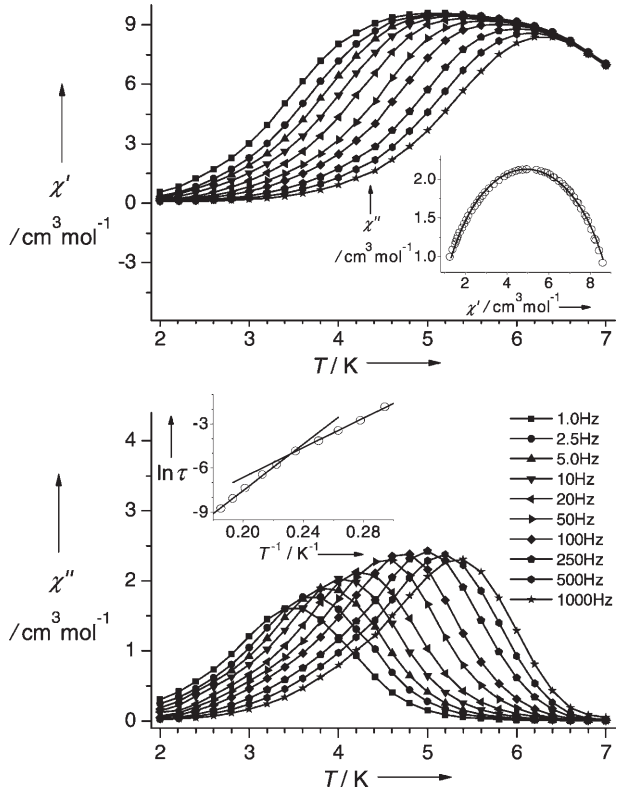

Figure 5. Top: Real part of ac susceptibility (inset: Cole–Cole diagram at 4.2 K). Bottom: Imaginary part of ac susceptibility (inset: peak temperatures of χ'' fitted by Arrhenius law for a powder sample of **2**).

ing linearly between 40 and 10 K with an energy gap of $\Delta_\xi/k_B = 24.0$ K (the value obtained by fitting the expression $\chi T = C_{eff}\exp(\Delta_\xi/k_B T)$ between 10 to 40 K). In theory, the energy gap obtained by fitting the plot of $\ln(\chi T)$ versus $1/T$ should be equal to $\Delta_{\tau 1} - \Delta_{\tau 2}$.[22e] Some disagreement seems to exist compared to the previous perfect examples.[3b,h,22a] The obtained Δ_ξ values are probably indicative of a wide distribution of chain lengths or just within the reasonable scope of the experimental error, in accord with some previous reports.[3a,j] In addition, the peak temperatures T_p of χ' can be measured by the parameter $\phi = (\Delta T_p/T_p)/\Delta(\lg f) = 0.10$,[23] which is in the range of normal superparamagnets and precludes the possibility of a spin glass. Moreover, the shape of the Cole–Cole diagram (inset of Figure 5, top) obtained at 4.2 K, which can be fitted by a generalized Debye model with an α value of 0.10, indicates a narrow distribution of relaxation time,[24] in agreement with the observed crossover behavior.

In summary, the above evidence reveals an interesting SCM behavior for **2**. Such behavior is mainly caused by the strong anisotropic intrachain ferromagnetic interactions that significantly "freeze" the magnetization in one direction and prevent easy reversal of the spins or 3D ordering behavior induced by interchain interactions. More importantly, the covalent-linking strategy described here should be suitable for preparing other SCMs. Longer σ-bonding linkers should be better suited to obtaining ideal SCM behavior.

Experimental Section

2: In a typical hydrothermal reaction, a mixture of $CoCl_2{\cdot}6H_2O$ (0.237 g, 1 mmol), 1,2-chdcH_2 (0.172 g, 1 mmol), and triethylamine (0.200 g, 2.0 mmol) in deionized water (10 mL) was sealed in a 23-mL teflon-lined autoclave and heated at 160 °C for 5 d to give dark red platelike crystals of **2** (87% yield), which was verified by powder XRD to be a pure phase (Figure S6). IR data for **2**: $\tilde{\nu} = 2928$ (m), 2957(w), 1600 (vs), 1540 (s), 1448 (s), 1417 (s), 1336 (w), 1290 (w), 1238 (w), 1116 (w), 1039 (w), 932 (w), 860 (w), 773 (w), 707 (m), 615 (w), 529 (w), 447 cm^{-1} (w). Elemental analysis (%) calcd for **2**: C 41.94, H 4.40; found: C 41.88, H 4.38. A large single crystal of **2** (8.0 mg, $3.7 \times 2.1 \times 0.4$ mm, see Figure S7) used in anisotropic magnetic measurements was grown in one month.

Crystal data of **2**: triclinic, $P\bar{1}$ (no. 2); $a = 5.1528(4)$, $b = 6.5380(6)$, $c = 13.366(1)$ Å, $\alpha = 99.260(1)$, $\beta = 97.900(1)$, $\gamma = 102.229(1)°$, $V = 427.42(6)$ Å^3, $Z = 2$, $\rho = 1.78$ g cm^{-3}, $\mu = 1.98$ mm^{-1}, final $R_1 = 0.0473$ for $I \geq 2\sigma(I)$, $wR_2 = 0.1352$ for all data. The intensity data were recorded on a Bruker SMART Apex CCD system with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL. CCDC-601744 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic susceptibility measurements on **2** were performed with a Quantum Design MPMS-XL7 SQUID. Hysteresis loops were measured in the "hysteresis mode". Data were corrected for the diamagnetic contribution calculated from Pascal constants.

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