A two-step field-induced magnetic transition in spin-canted systems observed only for the $\mathrm{Co^{II}}$ coordination polymer†

Hong-Peng Jia, Wei Li, Zhan-Feng Ju and Jie Zhang*

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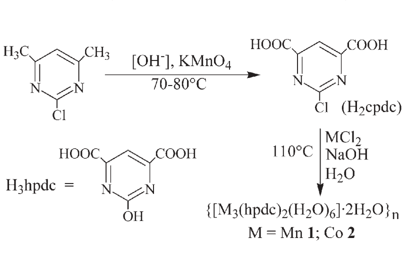
Two isostructural 1D compounds $\{[M_3(hpdc)_2(H_2O)_6]\cdot 2H_2O\}_n$ (M = Mn, Co; H_3hpdc = 2-hydroxypyrimidine-4,6-dicarboxylic acid) were synthesized by the *in situ* hydrothermal reactions of 2-chloropyrimidine-4,6-dicarboxylic acid with MCl_2 (M = Mn, Co) and NaOH; the $\mathrm{Mn^{II}}$ compound shows spin-canted antiferromagnetism, whereas the $\mathrm{Co^{II}}$ compound exhibits the coexistence of spin-canting and a two-step field-induced magnetic phase transition.

Molecule-based magnetic materials have attracted considerable attention due to their impressive structural diversity and intriguing physical properties as well as complicated magneto-structural correlations.[1] One of the major challenges in the area of molecular magnetism is the construction of magnetic frameworks with a spontaneous magnetization. Several different strategies are currently employed in order to achieve such magnetic entities.[2] However, it still remains difficult to design and synthesize molecular materials with predictable magnetic properties because the structural factors governing the exchange coupling between paramagnetic centers are complex and elusive. One origin for a spontaneous magnetization may arise from the noncollinear spin arrangements on two sub-lattices of an antiferromagnet, namely spin-canting.[3] Two contributions are necessary for spin-canting: (1) the presence of two non-symmetry related nearest neighbor magnetic ions and (2) antisymmetric exchange and/or single-ion anisotropy.[2a] If a ligand had predicable asymmetric coordination sites, it would be very beneficial for the occurrence of spin-canting. One successful example is a three-dimensionl (3D) homometallic molecular metamagnet with spin-canting constructed from the 3-hydroxypicolinate ligand with asymmetric coordination modes.[4] Despite the fact that a great amount of molecule-based magnetic materials with the spin-canting effect has been reported, exploration relevant to this strategy has been less so far. Herein, we report the first crystallographically characterized 1D metal complexes of the *in situ* generated H_3hpdc ligand with asymmetric coordination sites, $\{[M_3(hpdc)_2(H_2O)_6]\cdot 2H_2O\}_n$ (M = Mn, **1**; Co, **2**; H_3hpdc = 2-hydroxypyrimidine-4,6-dicarboxylic acid). It is interesting to note that **1** shows the expected spin-canted antiferromagnetism, whereas **2** shows the coexistence of spin-canting and a two-step field-induced magnetic transition. Until now, the simultaneous presence of spin-canting and metamagnetism in one system are still rare;[5] **2** is a unique example simultaneously showing spin-canting and a two-step field-induced magnetic phase transition.

2-Chloropyrimidine-4,6-dicarboxylic acid (H_2cpdc) could be prepared by oxidizing 2-chloro-4,6-dimethylpyrimidine in aqueous solution.[6] Crystals of **1** and **2** were only obtained by the *in situ* hydrothermal reactions of H_2cpdc with hydrated $MnCl_2/CoCl_2$ and NaOH in aqueous solution at 110 °C for 3 days (Scheme 1).‡ It should be pointed out that the 2-site halogen of H_2cpdc has high activity and can be replaced by an –OH group under hydrothermal conditions, giving the ligand H_3hpdc. Single-crystal X-ray diffraction§ reveals that **1** and **2** are isostructural 1D coordination polymers. Here, the structure of **2** is discussed as representative. The asymmetric unit of **2** contains two crystallographically unique Co atoms, one $\mathrm{hpdc^{3-}}$ anion, three coordinated and one lattice water molecules (Fig. S3, ESI†). Co1 is coordinated in a slightly distorted octahedral geometry with a NO_3 donor set coming from three different $\mathrm{hpdc^{3-}}$ ligands and two H_2O molecules. The Co2 atom also shows an octahedral geometry formed by two O and two N atoms of two different $\mathrm{hpdc^{3-}}$ ligands and two H_2O molecules. Co1 and Co2 are connected *via* a μ_2-carboxylate O atom and the –OCN– species of the $\mathrm{hpdc^{3-}}$ ligand to form a trinuclear unit, and each $\mathrm{hpdc^{3-}}$ bridges four $\mathrm{Co^{II}}$ ions in μ_4-mode, resulting in a 1D chain extending along the *c* axis (Fig. 1). Abundant hydrogen bonds among free water molecules, coordinated water molecules and the carboxylate oxygens hold adjacent chains together into a 3D supramolecular framework (Fig. S4, Table S1, ESI†). It is noticed that the NO_3 and N_2O_2 equatorial planes of $\mathrm{Co^{II}}$ ions within the trinuclear units are tilted with a dihedral angle of 18.41° and the shortest intraunit Co···Co distance is 3.741 Å, which have some influence on the magnetic properties of the complexes.

Both **1** and **2** display spin-canted magnetic behavior. A plot of $\chi_m T$ *vs.* T per Mn_3 unit under an applied field of 5 kOe for **1** is shown in Fig. 2a. Upon cooling, the $\chi_m T$ value decreases smoothly to *ca.* 75 K and then drops quickly to 4.82 cm^3 K mol^{-1} at 5 K. The temperature dependence of the reciprocal susceptibility (χ_m^{-1}) above 10 K obeys the Curie–Weiss law with a Weiss constant of $\theta = -10.4$ K, indicating dominant antiferromagnetic interactions.



Scheme 1

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter and Graduate School of the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: zhangjie@fjirsm.ac.cn; Fax: (+86) 591-83710051

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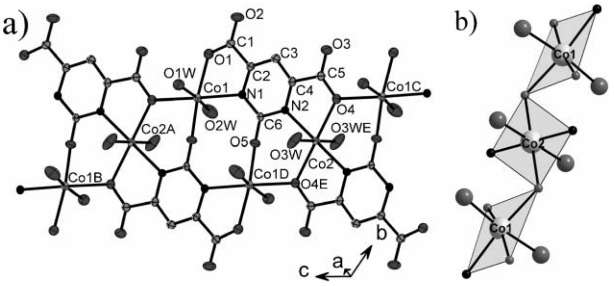

Fig. 1 (a) Crystal structure of **2** showing complete coordination environments of Co^{II} ions. Free water molecules and H atoms were omitted for clarity. (b) Schematic representation of the trinuclear unit in **2** showing vertex-sharing octahedra with slanted basal plane and different coordination environments.

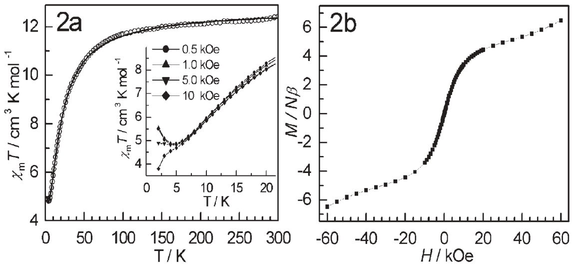

Fig. 2 (a) Plot of $\chi_m T$ *vs.* T for **1** at 5 kOe, the solid line is the best theoretical fit. Inset: the $\chi_m T$ *vs.* T plots under different fields at low temperature. (b) Field dependence of the magnetization of **1** at 2 K.

Below 5 K, the $\chi_m T$ curve shows a little rise, which is field dependent and disappears at higher field (the inset of Fig. 2a). Such behavior can well be expected for a canted spin system.[7] The antisymmetric exchange between adjacent Mn^{II} centers and the slanted equatorial planes of Mn^{II} ions within the chain should be mainly responsible for this canting effect due to the isotropic character of the high spin Mn^{II} ion.[8] The magnetization value reaches 6.48 $N\beta$ per Mn_3 unit at 60 kOe (Fig. 2b), much less than the expected saturation value of 15 $N\beta$ for three Mn^{II} ions with $S = 5/2$ and $g = 2$, consistent with its observed spin-canted behavior. On the basis of the structural data, **1** was considered to be approximately a uniform chain formed by the trinuclear Mn^{II} subunits. Therefore, the 1D chain can be treated as uniform Mn^{II} trimers with different intratrimeric (J) and intrachain (Jc) exchange constants.[9] Using this model, the magnetic data were well fitted in the temperature range 2–300 K with the best parameters $J = -0.88$ cm^{-1}, Jc = +0.04 cm^{-1}, and $g = 1.97$. The negative J value suggests a pronounced intratrimeric antiferromagnetic interaction between the Mn^{II} ions through the μ_2-carboxylate O and the –OCN– bridges.

Fig. 3a shows the $\chi_m T$ *vs.* T plots of **2** under different magnetic fields. At room temperature the $\chi_m T$ value is 9.63 cm^3 K mol^{-1}, which is significantly higher than the spin-only value of 5.63 cm^3 K mol^{-1} expected for three magnetically isolated Co^{II} ions with $S = 3/2$ and hence indicates a large orbital contribution arising from the high-spin octahedral Co^{II} centers.[2] On lowering temperature, $\chi_m T$ undergoes a gradual decrease down to 4.69 cm^3 K mol^{-1} around 16 K due to the spin–orbit coupling of the Co^{II} ions as well as possible antiferromagnetic interactions between the Co^{II} ions. Below 16 K, the $\chi_m T$ product increases rapidly to a sharp maximum of 9.22 cm^3 K mol^{-1} at 5 K and finally drops abruptly again. The maximum of $\chi_m T$ at low temperature decreases with increasing applied field (the inset of Fig. 3a); this field-dependent magnetic behavior is characteristic of spin-canting. The further decrease below 5 K may be attributed to interchain antiferromagnetic interactions and/or the zero-field splitting of the anisotropic high-spin Co^{II} ions.[10]

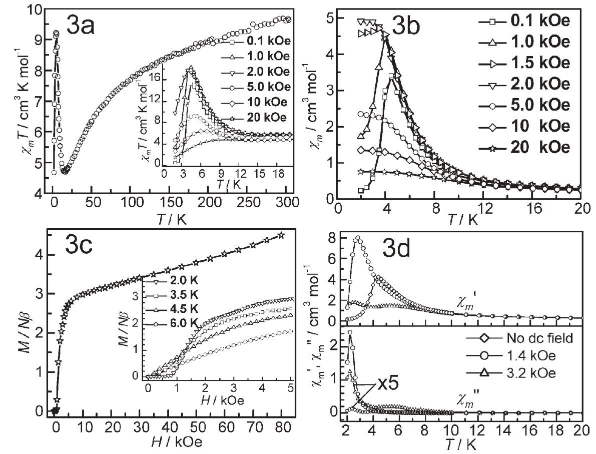

Fig. 3 (a) Plot of $\chi_m T$ *vs.* T for **2** at 5 kOe. Inset: $\chi_m T$ *vs.* T plots under different fields at low temperature. (b) Plots of χ_m *v.s* T for **2** at various fields. (c) Field-dependent magnetization of **2** at 2 K. Inset: the blow up of magnetization curves at different temperatures in the low field region. (d) Temperature dependence of the ac magnetic susceptibility of **2** measured in a field amplitude of 3 Oe and dc bias fields of 0, 1.4 and 3.2 kOe.

The χ_m *vs.* T curves show maxima around 4.5 K below an applied field of 2 kOe, which disappear at high field (Fig. 3b), suggesting an antiferromagnetic ordering at low field and the occurrence of a field-induced magnetic transition. The T_N value estimated from the maximum of d($\chi_m T$)/dT is 4.9 K. Further experimental evidence for the spin-canted weak ferromagnetism and magnetic phase transition in **2** comes from field-dependent isothermal magnetization measurements (Fig. 3c). The magnetization at 2 K displays a drastic rise in M *vs.* H at low field ($H <$ 6 kOe), and then increases at a slower rate in an almost linear fashion. The magnetization value of 4.49 $N\beta$ per Co_3 unit at the highest field (80 kOe) is far below the expected saturation value of 6.2–7.5 $N\beta$ for three Co^{II} ions in an octahedral environment with $S_{eff} = 1/2$ and $g = 4.1$–5.0,[11] but higher than that (2.1–2.5 $N\beta$) with an antiparallel arrangement of spins, consistent with spin-canted antiferromagnetism. A hysteresis loop is observed at 2 K with a coercive field (Hc) of 30 Oe and remnant magnetization of 0.002 $N\beta$ (Fig. S7, ESI†). Different from **1**, a two-step magnetic phase transition at low field is observed unexpectedly in **2**. The first transition occurs at *ca.* 1.3 kOe, determined by the dM/dH derivative curve (Fig. S8, ESI†). The isothermal magnetization curve below 2.5 kOe has an S-shaped curve, typical for a metamagnetic transition from the spin-canted antiferromagnetic state to a ferromagnetic-like state. The second step of the transition occurs at *ca.* 3.3 kOe, suggesting a complex magnetic phase diagram is involved in **2**. To date, there are several Co^{II} complexes in which a two-step field-induced magnetic phase transition has been observed.[11c,12] The second step transition in some of them is apt to be ascribed to a spin-flop phase transition although a spin-flop in such a system with large anisotropy is not traditional. The field dependent ac magnetic susceptibility measurement of **2** at 2 K reveals two maxima around 1.4 and 3.2 kOe in the $\chi_m'(H)$ plot (Fig. S9, ESI†), in agreement with the occurrence of a two-step magnetic phase transition. However, the appearance of a shoulder peak around 3.2 kOe for the imaginary component χ_m'' is different from the observation of the spin-flop effect,[11c,13] suggesting another ferromagnetic-like state may be involved due to the spin-reorientation upon enhancing the external applied field. In contrast to the bistable magnetic Co-PDBC complex with field-induced reorientation of the spins,[12b] the critical field of the second-step phase transition in **2** is much lower than that in the Co-PDBC complex (>15 kOe).

To further inspect the underlying magnetic nature of **2**, the measurements of ac magnetic susceptibilities at different dc bias fields were carried out (Fig. 3d). The zero-field ac magnetic susceptibility data exhibit a maximum value of χ_m' at 4.4 K with the absence of an imaginary component (χ_m'') at this temperature, consistent with the existence of antiferromagnetic ordering. However, the imaginary component χ_m'' presents a weak peak at 2.3 K, which is the signature of a magnetized state, thus indicating that a partly canted antiferromagnetic structure exists below this temperature.[4,14] No frequency dependence of the transition is observed. At an applied field of 1.4 kOe, the peak at 4.4 K disappears in the $\chi_m'(T)$ curve and a new peak appears around 2.8 K, accompanied by a maximum peak of χ_m'' at *ca.* 2.2 K. This feature is in accordance with a ferromagnetic-like state. When a dc field of 3.2 kOe is applied, the intensity of the real and imaginary components around 2.8 and 2.2 K decreases and additional new peaks appear around 5.4 K in χ_m' and χ_m'' *versus* T plots, corresponding to another ferromagnetic-like state resulting from a field-induced spin-reorientation.

In comparison with **1**, the magnetic behaviour of **2** is complicated in the low-temperature range and the spin-canting effect is more obvious, which is mainly due to the fact that Co^{II} ions inherently are much more anisotropic than Mn^{II} ions.[3] The occurrence of spin-canting usually is caused by single-ion magnetic anisotropy and/or antisymmetric magnetic exchange.[2a] For the two isostructural systems, the isotropic exchange and the antisymmetric one can be regarded as having the same magnitude,[15] therefore it should be the local anisotropy of the Co^{II} ions that make an additional contribution to a large degree of spin-canting. Different from the isomorphous 3D Co^{II} and Ni^{II} coordination polymers constructed from 2,1,3-thiadiazole-4,5-dicarboxylate,[15] in which the spin-canting effect is only observed in the Co^{II} complex, both of **1** and **2** in the present system show spin-canting. This magnetic difference relates to their structural features. Although there are also two crystallographically independent metal ions in the asymmetric unit of the former, the coordination environments of these two ions are quite similar, therefore the contribution of the asymmetric exchange interaction is expected to be small and the local anisotropy is the dominant factor which determines the presence or not of the canting phenomenon. By contrast, the NO_5 and N_2O_4 coordination environments and the tilted equatorial planes around the adjacent metal ions in **1** and **2** may favor the occurrence of the asymmetric exchange interactions and spin-canting.

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Notes and references

‡ Synthesis of **1** and **2**: An aqueous solution (4 ml) of H_2cpdc (20 mg) was adjusted to pH = 7 by dilute NaOH solution, then solid $MCl_2 \cdot nH_2O$ (24 mg, M = Co, n = 6; 20 mg, M = Mn, n = 4) was added and stirred for 20 min. The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 110 °C for 72 h, and then cooled to room temperature. Light yellow block crystals of **1** (yield: 53%) and red block crystals of **2** (yield: 38%) were obtained. EA: Calc. for $C_{12}H_{18}Mn_3N_4O_{18}$ **1**: C, 21.48; H, 2.70; N, 8.35. Found: C, 21.90; H, 2.90; N, 8.64%. Calc. for $C_{12}H_{18}Co_3N_4O_{18}$ **2**: C, 21.10; H, 2.66; N, 8.20. Found: C, 20.45; H, 2.87; N, 7.77%.

§ *Crystal data*: For **1**: $C_{12}H_{18}Mn_3N_4O_{18}$, M_r = 671.12, triclinic, $P\bar{1}$, a = 7.499(4), b = 9.246(5), c = 9.374(5) Å, α = 112.158(2), β = 107.435(4), γ = 100.623(4)°, V = 540.8(5) $Å^3$, Z = 1, D_c = 2.061 g cm^{-3}, μ = 1.826 mm^{-1}, F(000) = 337, GOF = 1.066, a total of 4202 reflections were collected, 2410 of which were unique (R_{int} = 0.0170). R_1 (wR_2) = 0.0282 (0.0905) for 169 parameters and 2410 reflections ($I > 2\sigma(I)$). CCDC 661336. For **2**: $C_{12}H_{18}Co_3N_4O_{18}$, M_r = 683.09, triclinic, $P\bar{1}$, a = 7.3879(19), b = 9.073(2), c = 9.1324(18) Å, α = 112.463(5), β = 106.946(6), γ = 99.518(5)°, V = 513.9(2) $Å^3$, Z = 1, D_c = 2.207 g cm^{-3}, μ = 2.499 mm^{-1}, F(000) = 343, GOF = 1.042, a total of 3973 reflections were collected, 2312 of which were unique (R_{int} = 0.0210). R_1 (wR_2) = 0.0378 (0.1015) for 169 parameters and 2312 reflections ($I > 2\sigma(I)$). CCDC 661337. Data were collected on a Rigaku Saturn70 CCD diffractometer for **1** and Rigaku Mercury CCD diffractometer for **2** equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The CrystalClear program was used for the absorption correction. All structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX97 program package. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714678g

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