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Linking cyano-bridged ladders by azide to form a layered metamagnet†

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Cyano-bridged corrugated ladder-like chains are connected by $\mu_{1,1}$–N_3 (end-on, EO) bridges to form a layered coordination polymer, $\{Mn(N_3)(CH_3OH)[Cr(phen)(CN)_4]\}\cdot CH_3OH$ (2), which is the first mixed cyano–azide bridged compound, and shows metamagnetism below 21.8 K, a temperature much higher than that (3.4 K) of the crossed double chain $[Cr(phen)(CN)_4]_2 [Mn(H_2O)_2]\cdot 4H_2O$ (1) based on the same building block $[Cr(phen)(CN)_4]^-$.

The use of hexacyanometallates of the type $[M(CN)_x]^{n-}$ (where M is a paramagnetic metal center) as building blocks for the construction of coordination polymers continues to be an important strategy in the field of molecule-based magnets.[1] An alternative approach is to use building blocks of the type $[M(CN)_x L_y]^{n-}$ (M = Fe[III], Cr[III], Mn[III], Ru[III], L = chelating ligand, and x = 2, 3, 4), which may result in compounds of different structures and properties.[2–3] We report here the construction of novel bimetallic Cr[III]–Mn[II] coordination polymers using the tetracyanometallate, $[N(CH_3)_4] [Cr(phen)(CN)_4]$,[4] as a building block. Reaction of $[N(CH_3)_4] [Cr(phen)(CN)_4]$ with Mn^{2+} is found to produce a bimetallic crossed-zigzag-chain complex, $[Cr^{III}(phen)(CN)_4]_2[Mn^{II}(H_2O)_2]\cdot 4H_2O$ (1), which is analogous to the $[Fe_2M]$ complex constructed from $[Fe^{III}(phen)(CN)_4]^-$ and Mn^{2+}.[3] We then figure if we can link up the chains by using an additional bridging ligand to replace the coordinated H_2O molecules on Mn^{II}, this should form a 2D network with stronger magnetic interactions and hence with a higher critical temperature. Indeed we found that when we react $[N(CH_3)_4][Cr(phen)(CN)_4]$ with Mn^{2+} in the presence of azide, a unique 2D compound, $\{Mn(N_3)(CH_3OH)[Cr(phen)(CN)_4]\}\cdot CH_3OH$ (2) was isolated. To the best of our knowledge, this is the first example of a coordination polymer that contains both cyanide and azide bridges. Magnetic studies show that 1 and 2 are both metamagnets, and the critical temperature of 2 (21.8 K) is much higher than that of 1 (3.4 K), as expected.

Compound 1‡ is isostructural with $[Fe^{III}L(CN)_4]_2[M^{II}(H_2O)_2]\cdot 4H_2O$ (L = phen, 2,2′-bpy; M = Mn, Co, Zn),[3] which consists of 4,2-ribbon like chains,[5] and is made up of neutral cyanide-bridged crossed Mn^{II}–Cr^{III} double zigzag chains. Each $[Cr(phen)(CN)_4]^-$ unit uses two *cis*-cyanide groups to connect two Mn^{II}. Each octahedral Mn^{II} is linked to four $[Cr(phen)(CN)_4]^-$ units in the equatorial positions, and the two axial positions are occupied by two H_2O molecules (Fig. S1a†). The intrachain Cr⋯Mn, Cr⋯Cr and Mn⋯Mn separations are 5.32–5.37, 7.44 and 7.69 Å, respectively. Each chain interacts with four adjacent chains by crystallized water molecule mediated hydrogen bonds (Fig. S1b†), and the shortest interchain M⋯M separation is larger than 7.5 Å.

Compound 2† is made up of a neutral 2D layer of $\{Mn(N_3)(CH_3OH)[Cr(phen)(CN)_4]\}$ in the *ab* plane and solvent methanol molecules. As shown in Fig. 1a, each $[Cr(phen)(CN)_4]^-$ unit uses its two equatorial *cis*-cyanide groups and one axial cyanide to connect to three Mn^{II}, while the other axial cyanide

remains terminal, and each Mn^{II} is linked to three $[Cr(phen)(CN)_4]^-$ units through cyanide bridges and one Mn^{II} through two 1,1′-azide (EO) bridges. Thus, Cr^{III} and Mn^{II} are connected through cyanide bridges to give a 3,3-ladder like chain.[5] The neighbouring ladders are connected through two 1,1′-azide (EO) bridges on the closest Mn^{II} ions, forming a unique 2D layer structure (Fig. 1b). The average intralayer Cr⋯Mn and Mn⋯Mn separations are 5.45 and 3.53 Å, respectively. The shortest interlayer Cr⋯Cr, Cr⋯Mn and Mn⋯Mn distances are 7.49, 7.03 and 7.67 Å, respectively. There might be some π–π stacking interaction between the phen groups of adjacent layers (Fig. S2†). Clearly, the addition of N_3^- reduces the number of coordinated solvent molecules on Mn^{II}, alters the connecting mode of the building block $[Cr(phen)(CN)_4]^-$, and increases the dimensionality.

Temperature dependencies of the molar magnetic susceptibility χ_M of 1 ($Mn^{II}Cr^{III}_2$) and 2 ($Mn^{II}Cr^{III}$) are presented in Fig. 2a and Fig. 2b, respectively. For both compounds χ_M above 90 K obeys the Curie–Weiss law ($\chi_M = C/(T - \theta)$) and gives: $C = 7.81$ cm³ mol⁻¹ K, $\theta = -52.4$ K for 1, and $C = 6.60$ cm³ mol⁻¹ K, $\theta = -35.1$ K for 2. The C values of 1 and 2 are close to 8.125 and 6.25 cm³ mol⁻¹ K expected for spin-only ions in $Mn^{II}Cr^{III}_2$ and $Mn^{II}Cr^{III}$ (g = 2), respectively. The negative θ indicates a dominant antiferromagnetic (AF) coupling between Cr^{III} and Mn^{II} ions in 1 and 2. On lowering the temperature, the $\chi_M T$ values of 1 and 2 decrease gradually, reach a minimum at 14 and 54 K, respectively, then increase abruptly to a maximum at 5 and 18 K, respectively, characteristic of a ferrimagnetic behavior. Upon further cooling, $\chi_M T$ drops sharply, suggesting AF interactions between the ferrimagnetic chains in 1 or the layers in 2.

As shown in the inset of Fig. 2a, there is a maximum around 3.5–4 K in the χ_M *vs.* T curves measured at low field (0.2–5 kOe), which disappears at high field (>7.5 kOe); suggesting an AF
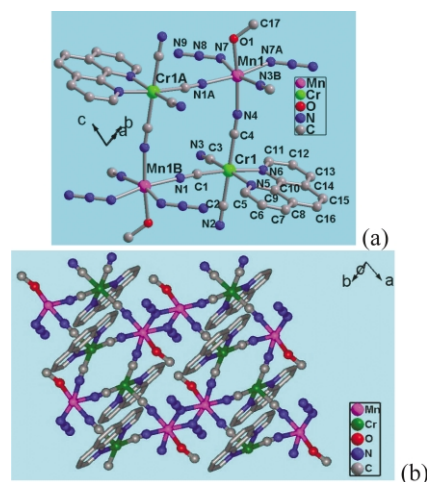

Fig. 1 Structure of 2. (a) View of the ladder including asymmetric unit with atom numbering. (b) Stick and ball view of *ab* plane showing the cyano and azido bridges between Cr^{III} and Mn^{II}; terminal cyano groups were neglected for clarity.

† Electronic supplementary information (ESI) available: crystal structure plots, more magnetic data and plots for 1 and 2. See http://www.rsc.org/suppdata/cc/b4/b405167j/

ordering at low field and a metamagnetic transition at high field. The AF transition is further evidenced by a peak at *ca.* 4 K of zero-field in-phase ac magnetic susceptibility $\chi'_M(T)$. T_N can be estimated to be 3.4 K from the maximum of $d(\chi'_M T)/dT$ (Fig. S3†). The magnetization of **1** at 1.8 K first increases slowly with increasing field, and then shows a sharp transition to a saturated value of 1.10 $N\beta$ (Fig. S4†), consistent with the expected value $S_T = (3/2 \times 2 - 5/2) = 1/2$ per MnCr$_2$ unit for a ferrimagnet state. The transition field from antiferromagnet to ferrimagnet at 1.8 K is *ca.* 5.5 kOe, estimated from the sharp peak of the field-dependent ac susceptibility (Fig. S4†).

Similar AF and AF–ferrimagnetic transitions are observed in **2** but at a much higher temperature. As shown in the inset of Fig. 2b, the χ_M *vs. T* plot at low field (0.2–3 kOe) displays a sharp peak at 21.8 K, which disappears at higher field (> 5 kOe), suggesting an AF state and a metamegnetic transition. The AF ordering is confirmed by the frequency-independent maximum of χ'_M at *ca.* 22.2 K; and T_N can be estimated to be 21.8 K by the peak position of $d(\chi'_M T)/dT$ (Fig. S5†). The field-dependent magnetization below T_N shows sigmoidal curves, confirming the metamagnetism of **2** (Fig. S6†). The saturation value of 2.29 $N\beta$ at 60 kOe and 1.8 K is consistent with a ferrimagnetic state with $S_T = 1$ per MnCr unit, as expected. The field-dependent ac susceptibility at 1.83 K shows a sharp peak at *ca.* 5 kOe, giving the critical field for the AF to metamagnet transition (inset of Fig. S6†).

The magnetic behaviors of **1** and **2** can be rationalized on the basis of their molecular structures. The noncompensation between the AF coupled Mn^{II} and Cr^{III} leads to a ferrimagnetic chain, similar to that of [Fe$_2$Mn]. As the intrachain Cr···Cr distance is quite large (7.44 Å) and without direct bridges, the magnetic interaction between Cr ions may be neglected. Consequently, the crossed double chains are equivalent to an alternating chain with $S_{Mn} = 5/2$ and $S'_{Cr} = 3$. The best fitting of the magnetic data above 5 K in terms of the alternating chain model[6] ($H = -JS_{Mn}S'_{Cr}$, where J is

the intrachain coupling) gives the parameters: $J = -4.7$ cm^{-1}, $zJ' = -1.8$ cm^{-1} ($z = 6$), $g_{Mn} = 1.98$ and $g'_{Cr} = 2.03$ with $R = 8.4 \times 10^{-4}$ {$R = \Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calcd}]^2/\Sigma(\chi_M T)_{obs}^2$}. The AF interactions between the nearest chains ($zJ' = -1.8$ cm^{-1}) result in an AF ground state, which turns to a ferrimagnetic state at higher fields, showing a metamagnetic behavior. In the 2D compound **2**, Mn^{II} and Cr^{III} are AF coupled through CN$^-$ in the ladder. Between the ladders, the Mn–N$_{azide}$–Mn angle of 103.3° is within the range of 100–105° for Mn^{II} azides,[7] which gives rise to ferromagnetic exchange interactions. Thus, the alignments of the spins of all Mn^{II} ions are parallel, but antiparallel to those of Cr^{III} ions; forming a $S_T = 1$ ferrimagnetic layer. The short interlayer separations (7.02–7.66 Å < 10 Å) are thought to enhance AF interlayer interactions, thereby giving rise to metamagnetic behavior.[8]

In summary, 1D [**1** (MnCr$_2$)] and 2D [**2** (MnCr)] metamagnets have been obtained by using the tetracyanometallate, [N(CH$_3$)$_4$][Cr(phen)(CN)$_4$], as the precursor. T_N of **2** is 6 times larger than that of **1** owing to the increase in dimensionality as a result of the second bridge—azide. This approach could lead to a new family of mixed cyano–azide bridged molecular magnets.

Notes and references

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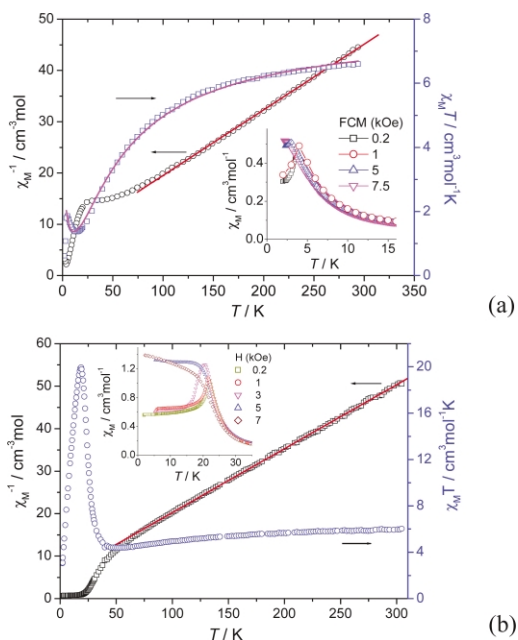8 M. Ohba, H. Ōkawa, N. Fukita and Y. Hashimoto, *J. Am. Chem. Soc.*, 1997, **119**, 1011.

Fig. 2 $\chi_M T$ and $1/\chi_M$ *vs. T* in an applied field: (a) for **1** at 1 kOe; (b) for **2** at 5 kOe. The red solid line corresponds to the best fit to the Curie–Weiss law, and the pink solid line corresponds to the best fit with an alternating-chain model. Insets: χ_M *vs. T* plots at different fields.