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Three-Dimensional Heterometallic Chiral Cr–Mn Compound Constructed by Cyanide and Dicyanamide Bridges

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Increasing the number of chiral centers by adjusting auxiliary coligands results in a heterometallic metamagnet with a three-dimensional homochiral framework containing both cyanide and dicyanamide bridges.

The design of chiral magnetic materials for combining magnetism and optical activity has been of active interest in recent years.[1−8] Especially, great efforts in constructing high-dimensional homochiral molecular magnets with long-range ordering have been prompted by the possibility of observing stronger magnetochiral dichroism (MChD).[3−8] In this regard, materials based on short bridges of oxalate ($C_2O_4^{2-}$, ox), cyanide (CN^-), or azide (N_3^-), the most effective mediators of magnetic couplings, are studied much more. A series of chiral ox-bridged compounds have been reported through $[M(ox)_3]^{3-}$ blocks.[4] Inoue and Gao have achieved some interesting chiral magnets bridged by hexacyanometalates or azides through two representative approaches: stereoselective synthesis using chiral species and spontaneous resolution upon crystallization with an achiral auxiliary, respectively.[5,7] Among the reported chiral magnets, cyano-bridged ones might be all-important because of the highest ordering temperatures. However, it is still an open challenge in constructing new ones by spontaneous resolution because of the serendipitous and unclear self-organization processes at present.

As mentioned previously, chiral units could be formed from achiral components simply by coordination or better by chelates. In the investigation on the cyano-bridged Cr−Mn system based on building blocks $[Cr(L)(CN)_4]^-$ (L = phen or 2,2′-bpy),[9] we also found that, although no chiral compounds were obtained, chiral units (such as dinuclear of [Cr1Mn1]) based on more than one auxiliary coligand did exist in the reported compounds, indicating possible *chiral induction* through the $[Cr(L)(CN)_4]^-$ units. However, the units were racemic by an inversion center in all of the compounds. Thus, the question is, how does one reduce the centrosymmetric probability and then extend ("*transfer*") chirality into high dimensions?

Although we have obtained a zigzag chain of $\{Mn(dca)(bpy)(H_2O)[Cr(bpy)(CN)_4]\cdot H_2O\}_n$ (**A**),[9b] the remarkable coordination diversities of the dicyanamide ($N(CN)_2^-$, dca) ligand[10] as well as its asymmetric character, which might be propitious to *chiral induction and transfer,* still attracted our further investigation on the $[Cr(bpy)(CN)_4]^-$/Mn^{II}/bpy/dca$^-$ system in detail. As a result, three new compounds $[\{Mn(bpy)(dca)(H_2O)_2[Cr(bpy)(CN)_4]\}\cdot CH_3OH$ (**1**), $\{Mn(dca)(H_2O)_2[Cr(bpy)(CN)_4]\}_n\cdot 2nH_2O$ (**2**), and $\{Mn(bpy)_{0.5}(dca)[Cr(bpy)(CN)_4]\}_n$ (**3**)] were obtained.[11] Among them, compound **3** shows a three-dimensional (3D) homochiral framework. Herein, we report their synthesis, structures, and magnetic properties.

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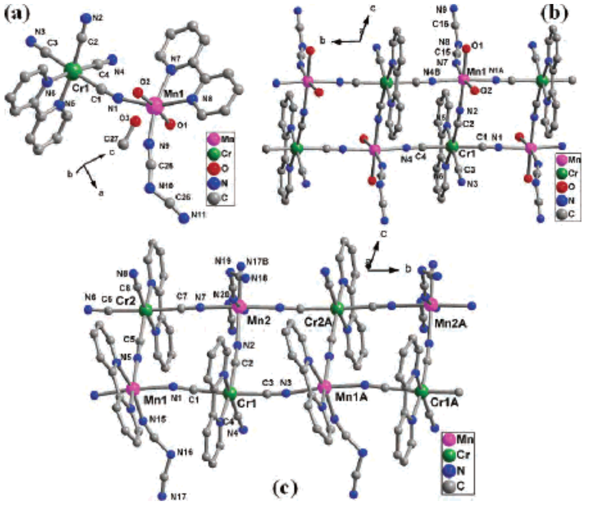

Figure 1. View of the structure of (a) a dinuclear unit of **1**, (b) a 3,3′-ladder-like chain of **2**, and (c) a homochiral 3,3′-ladder-like chain along the *bc* plane of **3**.

1 consists of a neutral molecular dinuclear entity of $\{Mn(bpy)(H_2O)_2(dca)[Cr(bpy)(CN)_4]\}$ and lattice methanol molecules (Figure 1a). The Cr^{III} ion chelated by one bpy is coordinated to four cyanide groups and connects to the octahedral Mn^{II} ion through one cyanide group ($\angle Mn1-N1\equiv C1 = 165.3°$). The other sites of the Mn^{II} ion are occupied by another bpy, two water molecules, and one terminal dca ligand, respectively. The dinuclear unit itself is chiral, but heterochiral units are centrosymmetrically linked into a 3D crystal structure in space group $P\bar{1}$ via H bonds between the dinuclear units (Figure S1 in the Supporting Information).

The structure of **2** consists of neutral cyano-bridged bimetallic 3,3′ ladders of $\{Mn(dca)(H_2O)_2Cr(bpy)(CN)_4\}_n$ (Figure 1b), similar to that of compound $\{Mn(N_3)(CH_3OH)(H_2O)[Cr(bpy)(CN)_4]\cdot 2H_2O\}_n$,[9b] where azide ligands are now replaced by terminal dca ligands. Each $[Cr(bpy)(CN)_4]^-$ unit connects to three octahedral Mn^{II} ions in *mer* geometry,[9b] and correspondingly each Mn^{II} ion is linked to three Cr^{III} ions by cyanide bridges, thus forming a planar ladder along the *b* axis. The other three sites of Mn1 are occupied by one N_{dca} (N7) and two O_{water} (O1 and O2) atoms with $Mn-N_{dca} = 2.19$ Å and $Mn-N_{cyanide} = 2.23-2.25$ Å. Again, upon coordination, the dinuclear $[Mn(dca)(H_2O)_2Cr(bpy)(CN)_4]$ unit is chiral but is heterochirally linked to the neighboring ones by the inversion center in the ladder. The Cr−Mn distances in the rungs and legs are slightly different, with 5.37 and 5.45−5.48 Å, respectively. The shortest interladder Cr−Cr, Cr−Mn, and Mn−Mn distances are ca. 8.0 Å. The ladders and lattice water molecules form a 3D crystal structure through lots of H bonds (Figure S2 in the Supporting Information).

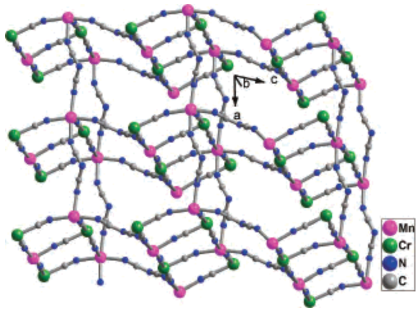

Figure 2. View of a homochiral 3D structure of **3** bridged by cyanide and $\mu_{1,5}$-dca ligands. (All bpy molecules are omitted for clarity.)

Compound **3** shows a novel homochiral 3D framework in space group P1. As shown in Figure 1c, the asymmetric unit, a chiral tetranuclear entity of $\{Mn_2(bpy)(dca)_2[Cr(bpy)(CN)_4]_2\}$, includes two unique Cr^{III} ions (Cr1 and Cr2) and two Mn^{II} ions (Mn1 and Mn2). $[Cr(bpy)(CN)_4]^-$ units and octahedral Mn^{II} ions are connected to each other in the same mode in **2**, giving a *bc*-planar 3,3′-ladder-like chain along the *b* axis. Each Cr1 links two Mn1 and one Mn2 ions, while each Cr2 connects two Mn2 and one Mn1 ions; thus, the two unique dinuclear units, [Cr1−Mn1] and [Cr2−Mn2], repeat, homochirally, along one leg of the ladder and along the other, respectively. The rest of the three coordination sites of Mn1 are completed by one bpy and one dca bridge (Mn1−N15 = 2.16 Å), while those of Mn2 by three dca bridges [Mn2−N17B(N18C, N20) ≈ 2.22 Å]. Thus, each Mn1 as a 4-connection site is further linked to one Mn2 ion of a neighboring ladder through a $\mu_{1,5}$-dca bridge, giving a homochiral two-dimensional sheet in the *bc* plane, which is homochirally extended into the final 3D structure by $\mu_{1,5}$-dca bridges from the 6-connected Mn2 ions (Figures 2and S3 in the Supporting Information). The dca-bridged Mn⋯Mn separations are 8.50 Å (Mn1⋯Mn2) and 8.73 Å (Mn2⋯Mn2), which are similar to those previously reported through $\mu_{1,5}$-dca bridges.[10]

It is noteworthy that our synthetic strategy is mainly based on the coordination abilities of the different auxiliary coligands (bpy > dca > H_2O). Thus, the rational decrease of bpy (half the amount, which released half the amount of Mn^{2+} ions for dca ligands) plays a crucial role in the formation of **3**, successfully inducing two different Mn sites, Mn1 ($[Mn(bpy)(NC)_3(dca)]$) and Mn2 ($[Mn(NC)_3(dca)_3]$), and thus leading to a chirally binded tetranuclear unit [Cr1Mn1Cr2Mn2]. Compared with **A**, **1**, and **2**, where only one dinuclear chiral unit ([Cr1Mn1]) exists, obviously, the centrosymmetric probability between the tetracenter units in **3** could reduce greatly. As a result, **3** represents a new example of *chiral induction and transfer*, from mixed achiral ligands to chiral tetranuclear units, to homochiral ladders by cyanide, and finally to 3D chiral framework by dca bridges. It seems that increasing the number of potential chiral centers

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(11) The Experimental Section is in the Supporting Information. Crystal data for **1**: $C_{27}H_{24}N_{11}O_3CrMn$, $M_r = 657.51$, triclinic, space group $P\bar{1}$, $a = 9.6018(3)$ Å, $b = 11.8578(4)$ Å, $c = 14.4407(6)$ Å, $\alpha = 85.8039(15)°$, $\beta = 85.1427(15)°$, $\gamma = 75.889(2)°$, $V = 1586.48(10)$ Å^3, $Z = 2$, and R1 and wR2 are 0.0389 and 0.0831, respectively, for 454 parameters and 3597 reflections [$I \geq 2\sigma(I)$]. Crystal data for **2**: $C_{16}H_{16}N_9O_4CrMn$, $M_r = 505.32$, triclinic, space group $P\bar{1}$, $a = 8.5369(2)$ Å, $b = 10.9222(3)$ Å, $c = 12.9272(5)$ Å, $\alpha = 101.0173(10)°$, $\beta = 95.5610(10)°$, $\gamma = 110.7018(12)°$, $V = 1088.85(6)$ Å^3, $Z = 2$, and R1 and wR2 are 0.0388 and 0.1089, respectively, for 296 parameters and 3387 reflections [$I \geq 2\sigma(I)$]. Crystal data for **3**: $C_{42}H_{24}N_{20}Cr_2Mn_2$, $M_r = 1022.69$, triclinic, space group P1, $a = 8.7335(3)$ Å, $b = 10.8480(3)$ Å, $c = 13.3950(5)$ Å, $\alpha = 70.2819(13)°$, $\beta = 76.1788(12)°$, $\gamma = 76.5467(11)°$, $V = 1143.89(6)$ Å^3, $Z = 1$, and R1 and wR2 are 0.0423 and 0.1073, respectively, for 595 parameters and 6706 reflections [$I \geq 2\sigma(I)$]. $\langle E^2 - 1\rangle = 0.791$ (expected 0.968 for centrosymmetric structures and 0.736 for noncentrosymmetric structures). The structures were solved and refined using the *SHELX-97* program.

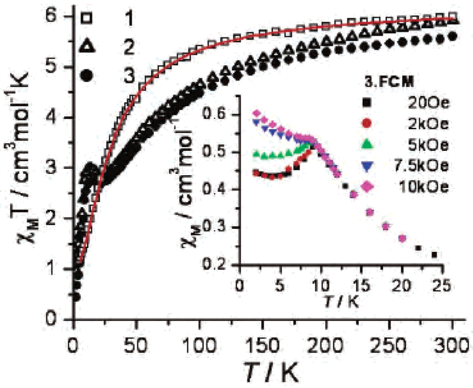

Figure 3. $\chi_M T$ vs T in an applied field of 1 kOe for **1** (□), 1 kOe for **2** (△), and 2 kOe for **3** (●). Inset: χ_M vs T plots at different fields for **3**.

in the unit by adjusting auxiliary coligands would be of benefit to the formation of chiral structures, and this has merit for further investigation.

The magnetic properties of **1**−**3** were investigated (Figures 3 and S4 in the Supporting Information). Their magnetic susceptibilities (per [MnCr] unit) above 50 K obey the Curie−Weiss law with the Curie (C) and Weiss (θ) constants: $C = 6.3$ cm^3 mol^{-1} K, $\theta = -19.5$ K for **1**; $C = 6.6$ cm^3 mol^{-1} K, $\theta = -46$ K for **2**; and $C = 6.4$ cm^3 mol^{-1} K, $\theta = -43$ K for **3**, respectively. The C values are in good agreement with the calculated value of 6.25 expected for a sum of isolated spin-only ions for $Mn^{II}Cr^{III}$ ($g = 2$). The negative Weiss constants indicate an overall antiferromagnetic (AF) interaction between Cr^{III} and Mn^{II} ions. The data of **1** were fitted by the dimer model with the best results ($H = -JS_{Cr1}\cdot S_{Mn1}$, where J and zJ' are the coupling constants through the cyano bridge and intermolecular interaction, respectively): $J = -5.2$ cm^{-1}, $zJ' = 0.15$ cm^{-1}, $g = g_{Cr} = g_{Mn} = 2.02$ with $R = 1.2 \times 10^{-5}$ $\{R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\sum(\chi_M T)_{obs}{}^2\}$.

Both **2** and **3** are metamagnets. Their $\chi_M T$ values decrease gradually upon cooling, reach minima at about 22 K, and then increase abruptly, indicating a ferrimagnetic-like character, which might be due to the noncompensation between the AF-coupled spins of the Mn^{II} and Cr^{III} ions in the ladders. The further sharp decreases after the maxima at about 14 and 16 K, respectively, might be caused by the magnetic saturation and/or AF interactions between the ladders. Long-range orderings were confirmed by field-cooled magnetizations (FCMs) and ac susceptibilities at different frequencies of 277−4111 Hz in a zero dc field (Figures S5−S7 in the Supporting Information). The FCMs at 100 Oe for **2** (Figure S5 in the Supporting Information) and at 20 Oe for **3** (inset of Figure 3) and the real parts of ac susceptibilities display maxima at about 3 and 9 K, respectively, while the out-of-phase component (χ'') remains zero, clearly indicating the occurrence of 3D AF ordering. The transition temperatures (T_N) were estimated as 2.8 K (for **2**) and 9 K (for **3**) by the peak of χ_{ac} vs T. The maxima in χ_M vs T plots gradually disappear when the applied fields are increased, suggesting a metamagnetic behavior.

The sigmoid-shaped field-dependent magnetization at 1.8 K shows that a field-induced metamagnetic transition occurs from an AF state to a ferrimagnetic state, where the magnetization value is 2.21 Nβ/mol at 70 kOe and 1.8 K for **2** and 2.01 Nβ/mol at 50 kOe and 1.9 K for **3**, consistent with the expected ferrimagnetic state with $S_T = {}^5/_2 - {}^3/_2 = 1$ for the [MnCr] unit (Figure 4). The critical field (H_c) is ca. 0.75 kOe for **2** at 1.8 K, greatly lower than that of **3** with 7.5 kOe, estimated from the sharp peak of dM/dH vs H. As expected, the sigmoidal feature of the magnetization curves gradually disappears at 5 and 10 K for **3**.

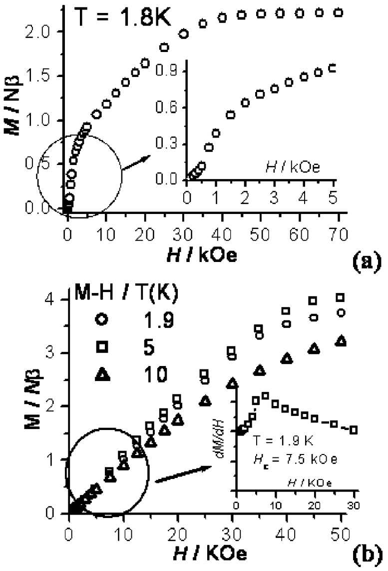

Figure 4. Field dependence of magnetization (a) for **2** at 1.8 K and (b) for **3** at 1.9, 5, and 10 K, respectively. Inset: low-field region.

It is reasonable that **3** as well as **2** shows metamagnetism because of different intraladder (cyano bridge) and interladder (through H bonds for **2** and a dca bridge for **3**) interactions. Moreover, although the interladder distances of **3** are slightly longer than those of **2**, the $\mu_{1,5}$-dca bridges exhibit more effective pathways in mediating magnetic coupling, leading to higher H_c and T_N.

In summary, we synthesized a series of cyano/dca-coordinated compounds based on the $[Cr(bpy)(CN)_4]^-$ unit as well as the different coordination abilities of bpy and dca. The insufficiency of bpy leads to the first 3D metamagnet (**3**) containing both cyanide and dca bridges, which is also a new example of *chiral induction and transfer*, from achiral components to homochiral solids. The present result indicates that increasing the number of potential chiral centers in the molecular unit by adjusting auxiliary coligands seems to be an effective way of avoiding heterochiraliy and undergoing spontaneous resolution.

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Supporting Information Available: CIF files, plots of crystal packing, more figures of magnetic data, and detailed crystallographic data (Table S1) and selected bond lengths and angles (Table S2) for the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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