

Heterometallic Cr–Mn Complexes Containing Cyanide and Oxalate Bridges

Yuan-Zhu Zhang, Zhe-Ming Wang, and Song Gao*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

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Three heterometallic Cr–Mn compounds, $\{\text{Mn}(\mu\text{-ox})_{0.5}(\text{H}_2\text{O})[\text{Cr}(\text{phen})(\text{CN})_4]\}_n \cdot n\text{H}_2\text{O} \cdot 2n\text{CH}_3\text{OH}$, (**1**), $\{\text{Mn}(\mu\text{-ox})_{0.5}(\text{H}_2\text{O})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_n \cdot 2n\text{H}_2\text{O} \cdot n\text{CH}_3\text{OH}$, (**2**), and $\{\text{Mn}(\mu\text{-ox})_{0.5}(\text{bpy})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_n$, (**3**) (ox = oxalate), containing cyanide and oxalate bridges based on building blocks $[\text{Cr}(\text{L})(\text{CN})_4]^-$ (L = phen and 2,2'-bipyridine) have been prepared. A new approach was first employed to synthesize ox-bridged compounds via facile oxidation-hydrolysis reactions of diaminomaleonitrile. X-ray crystallography revealed that the structures of **1** and **2** are similar, where cyano-bridged corrugated ladderlike chains are further connected through bis-bidentate oxalato bridges to unique two-dimensional layered structures. Of note is that the introduction of 2,2'-bipyridine led to an interesting cluster-based chainlike compound (**3**) with cyano-bridged squares $[\text{Mn}_2\text{Cr}_2]$ extended by ox bridges. Magnetic studies show antiferromagnetic (AF) interaction between cyano-bridged $\text{Cr}^{\text{III}}\text{--Mn}^{\text{II}}$ and ox-bridged $\text{Mn}^{\text{II}}\text{--Mn}^{\text{II}}$ ions, with the result that **1** and **2** exhibit AF ordering with spin-flop behaviors below 18 and 19 K, respectively.

Introduction

Molecular magnetic materials based on short bridges of cyanide (CN^-), azide (N_3^-), oxalate ($\text{C}_2\text{O}_4^{2-}$, ox), or dicyanamide $[\text{N}(\text{CN})_2^-]$, dca], which represent the most effective magnetic exchange transfers, have been investigated extensively, while respectively, in the past two decades or so, because of their abundant structural and magnetic diversities, these materials have formed the four most important families of molecular magnets.^{1–6} Till now, numerous zero- to three-dimensional (0D to 3D) complexes bridged by each of them have been described. However, combining two or more kinds of the above bridges in one

compound is still a challenge and of great interest for the rational design and construction of new molecular magnetic materials with special structures and interesting properties in regard to their individual advantages, both coordinated

* Author to whom correspondence should be addressed. Fax: (+86)-10-62751708. Tel: (+86)-10-62756320. E-mail: gaosong@pku.edu.cn.

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and magnetic. Escuer et al. used an ox-bridged dinuclear complex $[\text{Ni}_2(\text{dpt})_2(\mu\text{-ox})]$ [dpt = triamine bis-(3-aminopropyl)amine] as a precursor and synthesized the first 1D example containing ox and azide bridges in 1994.⁷ Then, a series of similar works were done over the following 10 years.⁸ Meanwhile, Muga et al. achieved the combination of cyanide and oxalate bridges together to obtain several trinuclear compounds $[\{\text{Ni}(\text{dien})\}_2(\mu\text{-ox})\{\mu\text{-M}(\text{CN})_4\}]$ ($\text{M} = \text{Ni}^{\text{II}}$, Pt^{II} , and Pd^{II}).⁹ Unfortunately, the cyanide blocks of square-planar $[\text{M}(\text{CN})_4]^{2-}$ units are diamagnetic.

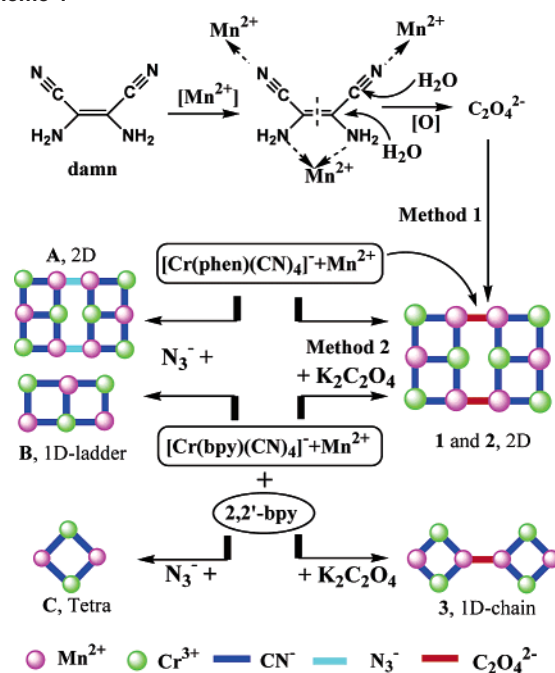
As we communicated the synthesis of a 2D bimetallic complex bridged by cyanide and azide with long-range metamagnetic ordering below 21.8 K, $\{\text{Mn}(\text{N}_3)(\text{CH}_3\text{OH})[\text{Cr}(\text{phen})(\text{CN})_4]\}_n \cdot n\text{CH}_3\text{OH}$ (**A**),¹⁰ we supposed that the alternative building blocks of $[\text{Cr}(\text{L})(\text{CN})_4]^-$ [$\text{L} = \text{phen}$ and 2,2'-bipyridine (2,2'-bpy)] might be the key to open hybrid systems containing cyanide and other effective bridging ligands. However, we only obtained one 3,3'-ladderlike^{1b} chain of $\{\text{Mn}(\text{N}_3)(\text{CH}_3\text{OH})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_n \cdot 2n\text{H}_2\text{O}$ (**B**), one square tetranuclear complex of $\{\text{Mn}(\text{bpy})(\text{N}_3)(\text{H}_2\text{O})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_2 \cdot 2\text{H}_2\text{O}$ (**C**), and one zigzag chain of $\{\text{Mn}(\text{dca})(\text{bpy})(\text{H}_2\text{O})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_n \cdot n\text{H}_2\text{O}$ (**D**) with a terminal azide or dca.¹¹

In the pursuit of continuing the combination of the above bridges, heterometallic compounds based on building blocks of $[\text{Cr}(\text{L})(\text{CN})_4]^-$ were further investigated by introducing oxalate through two different methods: a facile oxidation-hydrolysis reaction of diaminomaleonitrile (DAMN) as a steady oxalato creator (method 1) or a slow diffusion of an aqueous solution of $\text{K}_2\text{C}_2\text{O}_4$ into a water-methanol solution of MnCl_2 and $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{L})(\text{CN})_4] \cdot x\text{H}_2\text{O}$ (method 2) (Scheme 1). As a result, three heterometallic Cr-Mn compounds containing cyanide and oxalate bridges, $\{\text{Mn}(\mu\text{-ox})_{0.5}(\text{H}_2\text{O})[\text{Cr}(\text{phen})(\text{CN})_4]\}_n \cdot n\text{H}_2\text{O} \cdot 2n\text{CH}_3\text{OH}$ (**1**), $\{\text{Mn}(\mu\text{-ox})_{0.5}(\text{H}_2\text{O})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_n \cdot 2n\text{H}_2\text{O} \cdot n\text{CH}_3\text{OH}$ (**2**), and $\{\text{Mn}(\mu\text{-ox})_{0.5}(\text{bpy})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_n$ (**3**), were obtained. Herein, we report their synthesis, structures, and magnetic properties.

Experimental Section

General Remarks. All starting materials were commercially available, reagent grade, and used as purchased without further purification. Elemental analyses of C, H, and N were carried out on an Elementary Vario EL analyzer. The IR spectra were recorded against pure samples on a Magna-IR 750 spectrophotometer in the 4000–500 cm^{-1} region. The measurements of variable-temperature magnetic susceptibility and the field dependence of magnetization

Scheme 1



were performed on a Maglab²⁰⁰⁰ system and a Quantum Design MPMS XL-5 SQUID system.

Synthesis. The precursors $[\text{Cr}(\text{L})_2(\text{CN})_2][\text{Cr}(\text{L})(\text{CN})_4] \cdot \text{H}_2\text{O}$ were prepared by the reported method.¹² A mixture of the methanol solutions of molar equivalent $[\text{N}(\text{CH}_3)_4]\text{Cl}$ and $[\text{Cr}(\text{L})_2(\text{CN})_2][\text{Cr}(\text{L})(\text{CN})_4] \cdot \text{H}_2\text{O}$ gave stoichiometric crystalline products of mononuclear $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{phen})(\text{CN})_4] \cdot 0.5\text{H}_2\text{O}$ (crystallized in the $C2/c$ space group; anal. calcd for $\text{CrC}_{20}\text{H}_{21}\text{N}_7\text{O}_{0.5}$ (%): C 57.27, H 5.05, N 23.38; found: C 58.32, H 4.97, N 23.88) and $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{bpy})(\text{CN})_4] \cdot \text{H}_2\text{O}$ (anal. calcd for $\text{CrC}_{18}\text{H}_{22}\text{N}_7\text{O}$ (%): C 53.46, H 5.48, N 24.24; found: C 53.15, H 5.24, N 24.57).

1. Preparation of 1. Method 1. $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{phen})(\text{CN})_4] \cdot 0.5\text{H}_2\text{O}$ (0.2 mmol) and $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2 mmol) were dissolved in methanol/ H_2O (10:5 mL), then mixed with a bright solution of diaminomaleonitrile (1.0 mmol) in 5 mL of methanol. The resulting solution was stirred for about 20 min and then was filtrated and left to stand at room temperature. Yellow, blocked single crystals of **1** were obtained after 2 weeks. Yield: 40 mg, 37%. Elem Anal. for $\text{MnCrC}_{19}\text{H}_{20}\text{N}_6\text{O}_6$ (%): C, 42.63; H, 3.77; N, 15.70. Found: C, 41.97; H, 3.53; N, 16.13. IR stretching of oxalate and cyanide (cm^{-1}): 1650 [$\nu(\text{C}_2\text{O}_4^{2-})$, str] and 2166 [$\nu(\text{C}\equiv\text{N}^-)$, weak].

Method 2. An aqueous solution (3 mL) of $\text{K}_2\text{C}_2\text{O}_4$ (0.2 mmol) and 5 mL of water was put into a test tube in turn. Then, a well-mixed solution (5 mL of methanol and 2 mL of water) of $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{phen})(\text{CN})_4] \cdot 0.5\text{H}_2\text{O}$ (0.2 mmol) and MnCl_2 (0.2 mmol) was carefully laid above. Yellow, blocked single crystals of **1** were obtained after a month. Yield: 35 mg, 33%. Found: C, 42.02; H, 3.90; N, 15.50 (%). The crystals were confirmed by single-crystal X-ray analysis. The IR stretching results were the same as those of the products synthesized by method 1.

2. Preparation of 2. The preparation of **2** was carried out using a procedure similar to that employed for **1** with $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{bpy})(\text{CN})_4] \cdot \text{H}_2\text{O}$ in place of $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{phen})(\text{CN})_4] \cdot 0.5\text{H}_2\text{O}$. Yellow, blocked single crystals of **2** (yield: 41 mg, 41%, through method 1; yield: 30 mg, 30%, through method 2) were obtained after one month. Anal. Calcd for $\text{MnCrC}_{16}\text{H}_{18}\text{N}_6\text{O}_6$ (%): C, 38.64; H, 3.65;

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Table 1. Crystallographic Data for 1–3

| compound | 1 | 2 | 3 |
|--|---|---|---|
| formula | MnCrC ₁₉ H ₂₀ N ₆ O ₆ | MnCrC ₁₆ H ₁₈ N ₆ O ₆ | MnCrC ₂₅ H ₁₆ N ₈ O ₂ |
| M_r [g mol ⁻¹] | 535.34 | 497.29 | 567.40 |
| λ [Å] | 0.710 73 | 0.710 73 | 0.710 73 |
| T [K] | 293 | 293 | 293 |
| cryst syst | triclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ |
| a [Å] | 7.7927(2) | 7.9061(2) | 14.378(3) |
| b [Å] | 11.9503(3) | 11.9199(3) | 12.455(3) |
| c [Å] | 12.6843(4) | 12.5702(4) | 15.422(3) |
| α [deg] | 70.7925(10) | 66.3780(14) | 90 |
| β [deg] | 82.4865(10) | 80.6314(12) | 106.80(3) |
| γ [deg] | 78.227(2) | 80.0802(14) | 90 |
| V [Å ³] | 1089.42(5) | 1063.34(5) | 2643.9(9) |
| Z | 2 | 2 | 4 |
| ρ_{calcd} [mg m ⁻³] | 1.632 | 1.553 | 1.425 |
| $F(000)$ | 546 | 506 | 1148 |
| cryst size [mm ⁻¹] | 0.15 × 0.13 × 0.05 | 0.45 × 0.35 × 0.16 | 0.25 × 0.14 × 0.07 |
| $\mu(\text{Mo K}\alpha)$ [mm ⁻¹] | 1.128 | 1.149 | 0.926 |
| θ_{limit} [deg] | 3.4–28.03 | 3.4–27.5 | 3.40–24.10 |
| measured reflns | 21 418 | 18 737 | 30 426 |
| unique reflns | 5096 | 4877 | 4141 |
| observed reflns ^a | 3118 | 3368 | 2479 |
| no. of parameters | 318 | 297 | 279 |
| GOF | 0.991 | 1.026 | 0.924 |
| $T_{\text{max}}/T_{\text{min}}$ | 0.952/0.891 | 0.837/0.692 | 0.945/0.590 |
| $R1^b$ | 0.0474 | 0.0432 | 0.0457 |
| wR2 ^c | 0.1201 | 0.1158 | 0.0901 |
| larg. diff. P/h | 0.83/–0.73 | 0.80/–0.51 | 0.72/–0.41 |

^a Observation criterion: $I > 2\sigma(I)$. ^b $R1 = \sum |F_o| - |F_c| / \sum |F_o|$. ^c $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1–3

| | | 1 | | | |
|-------------------------|----------|-------------------------------|------------|-------------------------------|----------|
| Mn(1)–O(2) ^a | 2.165(2) | Cr(1)–C(4) | 2.065(4) | C(17)–O(2)–Mn(1) ^d | 116.0(2) |
| Mn(1)–N(1) ^b | 2.166(3) | Cr(1)–N(5) | 2.068(3) | C(1)–N(1)–Mn(1) ⁱ | 179.4(3) |
| Mn(1)–N(3) ^c | 2.188(3) | Cr(1)–C(3) | 2.068(4) | C(3)–N(3)–Mn(1) ^c | 173.0(3) |
| Mn(1)–O(1) | 2.189(2) | O(1)–C(17) | 1.244(4) | C(4)–N(4)–Mn(1) | 171.6(3) |
| Mn(1)–N(4) | 2.209(3) | O(2)–C(17) | 1.245(4) | N(1)–C(1)–Cr(1) | 174.9(3) |
| Mn(1)–O(3) | 2.212(3) | C(17)–C(17) ^a | 1.556(6) | N(2)–C(2)–Cr(1) | 176.2(3) |
| Cr(1)–C(1) | 2.037(4) | C(19)–O(5) | 1.265(10) | N(3)–C(3)–Cr(1) | 177.2(3) |
| Cr(1)–C(2) | 2.039(4) | O(4)–C(18) | 1.420(5) | N(4)–C(4)–Cr(1) | 179.2(3) |
| Cr(1)–N(6) | 2.056(3) | C(17)–O(1)–Mn(1) | 116.5(2) | | |
| | | 2 | | | |
| Mn(1)–N(2) ^d | 2.191(3) | Cr(1)–C(1) | 2.073(3) | C(15)–O(2)–Mn(1) ^e | 115.5(2) |
| Mn(1)–O(2) ^e | 2.202(2) | Cr(1)–C(3) | 2.094(3) | C(1)–N(1)–Mn(1) | 175.3(2) |
| Mn(1)–O(1) | 2.203(2) | O(1)–C(15) | 1.241(3) | C(2)–N(2)–Mn(1) ^d | 174.9(3) |
| Mn(1)–N(1) | 2.208(2) | O(2)–C(15) | 1.253(3) | C(3)–N(3)–Mn(1) ⁱ | 174.0(2) |
| Mn(1)–O(3) | 2.219(3) | O(5)–C(16) | 1.436(5) | N(1)–C(1)–Cr(1) | 174.7(3) |
| Mn(1)–N(3) ^f | 2.234(3) | C(15)–C(15) ^e | 1.561(5) | N(2)–C(2)–Cr(1) | 177.3(3) |
| Cr(1)–C(4) | 2.050(3) | O(2) ⁱ –Mn(1)–O(1) | 75.00(7) | N(3)–C(3)–Cr(1) | 177.9(3) |
| Cr(1)–N(6) | 2.057(2) | O(1)–Mn(1)–O(3) | 85.79(10) | N(4)–C(4)–Cr(1) | 176.2(3) |
| Cr(1)–C(2) | 2.060(3) | O(1)–Mn(1)–N(1) | 165.64(9) | | |
| Cr(1)–N(5) | 2.071(2) | C(15)–O(1)–Mn(1) | 115.7(2) | | |
| | | 3 | | | |
| Mn(1)–O(1) | 2.165(3) | Cr(1)–C(4) | 2.080(5) | C(25)–O(1)–Mn(1) | 116.2(2) |
| Mn(1)–N(1) | 2.189(4) | Cr(1)–C(1) | 2.082(5) | C(25)–O(2)–Mn(1) ^g | 115.0(2) |
| Mn(1)–O(2) ^g | 2.192(3) | Cr(1)–C(3) | 2.090(5) | C(1)–N(1)–Mn(1) | 152.5(4) |
| Mn(1)–N(4) ^h | 2.224(4) | O(1)–C(25) | 1.259(5) | C(4)–N(4)–Mn(1) ^h | 165.5(4) |
| Mn(1)–N(7) | 2.286(4) | O(2)–C(25) | 1.248(5) | N(1)–C(1)–Cr(1) | 174.0(4) |
| Mn(1)–N(8) | 2.291(4) | C(25)–C(25) ^g | 1.550(8) | N(2)–C(2)–Cr(1) | 177.5(4) |
| Cr(1)–C(2) | 2.042(5) | O(1)–Mn(1)–O(2) ^g | 75.61(10) | N(3)–C(3)–Cr(1) | 177.7(4) |
| Cr(1)–N(5) | 2.068(3) | O(1)–Mn(1)–N(4) ^h | 103.37(12) | N(4)–C(4)–Cr(1) | 176.3(4) |
| Cr(1)–N(6) | 2.073(3) | O(1)–Mn(1)–N(7) | 157.57(12) | | |

^a $-x + 1, -y + 1, -z$. ^b $x - 1, y, z$. ^c $-x + 1, -y + 2, -z$. ^d $-x + 1, -y + 1, -z + 2$. ^e $-x, -y + 2, -z + 2$. ^f $x - 1, y, z$. ^g $-x, -y + 1, -z$. ^h $-x, -y, -z$. ⁱ $x + 1, y, z$. ^j $x + 1, y, z$.

N, 16.90. Found: C, 39.26; H, 3.64; N, 17.16 (method 1) and C, 39.89; H, 3.71; N, 17.45 (method 2). IR stretching of oxalate and cyanide (cm⁻¹): 1648 [$\nu(\text{C}_2\text{O}_4^{2-})$, str] and 2164 [$\nu(\text{C}\equiv\text{N}^-)$, weak].

3. Preparation of 3. A well-mixed solution (5 mL of methanol and 5 mL of water) of $[\text{N}(\text{CH}_3)_4][\text{Cr}(\text{bpy})(\text{CN})_4] \cdot \text{H}_2\text{O}$ (0.2 mmol),

2,2'-bpy (0.2 mmol), and MnCl_2 (0.2 mmol) was poured into a 10 mL beaker. Then, the beaker, sealed by film with several pinholes, was deposited into a 50 mL beaker with an aqueous solution of 0.2 mmol of $\text{K}_2\text{C}_2\text{O}_4$ (about 40 mL). Yellow crystals were collected after 2 weeks. The crystals were dissolved under reflux for half an

hour in 10 mL of methanol and 10 mL of water, and then, the resulting solution was filtrated and left to stand at room temperature. Yellow, blocked crystals of **3** were isolated about a month later. Yield: 19 mg, 17%. Anal. Calcd for $\text{MnCrC}_{25}\text{H}_{16}\text{N}_8\text{O}_2$ (%): C, 52.92; H, 2.82; N, 19.75. Found: C, 53.03; H, 3.16; N, 19.80. IR stretching of oxalate and cyanide (cm^{-1}): 1643 [$\nu(\text{C}_2\text{O}_4^{2-})$, str] and 2156 [$\nu(\text{C}\equiv\text{N}^-)$, medium]. The sample used in the magnetic measurements has been confirmed by powder X-ray diffraction XRD analysis. (Figure S2 of the Supporting Information)

X-ray Crystallographic Study. The diffraction data collections of **1–3** were made at 293 K on a Nonius Kappa-CCD diffractometer. The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least squares (SHELXL-97) on F^2 . Anisotropic thermal parameters were used for the non-hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model.

CCDC-280738 to -280740 contain the supporting crystallographic data for this paper. They can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U. K.; fax: (international) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

Description of Crystal Structures. The detailed crystallographic data for all of the compounds are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

Description of the Structures of 1 and 2. The skeleton structures of **1** and **2** are similar to that of compound **A**, while the double end-on azido bridges are now replaced by oxalato bridges. Both structures (Figures 1a and 2a) consist of neutral 2D layers of $\{\text{Mn}(\mu\text{-ox})_{0.5}(\text{H}_2\text{O})[\text{Cr}(\text{L})(\text{CN})_4]\}_n$ along the ab plane and solvent molecules of water and methanol. The $[\text{Cr}(\text{L})(\text{CN})_4]^-$ building block uses its two equatorial *cis*-cyanide groups and one axial cyanide (fac geometry¹¹) to connect three Mn^{II} ions, while the other axial cyanide remains terminal. Accordingly, each six-coordinated Mn^{II} ion is linked to three $[\text{Cr}(\text{L})(\text{CN})_4]^-$ units through cyanide bridges. Thus, Cr^{III} and Mn^{II} are connected through cyanide to give a 3,3'-ladderlike^{1b} chain. The neighboring Mn^{II} ions between the ladders are further linked through bis-bidentate oxalato bridges, resulting in the unique 2D layer structure. The last coordination site of the Mn^{II} ion is occupied by a water molecule. The bridged $\text{Mn}-\text{N}\equiv\text{C}$ angles range from 171.6 to 179.4°, comparable to those in compound **A**. The shortest intralayer $\text{Cr}\cdots\text{Mn}$ and $\text{Mn}\cdots\text{Mn}$ separations are 5.33 and 5.69 Å for **1** and 5.41 and 5.72 Å for **2**, respectively. The $\text{Mn}\cdots\text{Mn}$ distances are consistent with those previously reported for the bis-bidentate oxalato bridge.^{13–15} The layers, with phen or bpy on both sides, interdigitate one to another, and the overlap of interlayer phen \cdots phen (for **1**) or bpy \cdots bpy (for **2**) distances with interplanar distances of 3.4–3.6 Å suggests π - π stacking between these planar aromatic moieties (Figures 1b and 2b).¹⁶

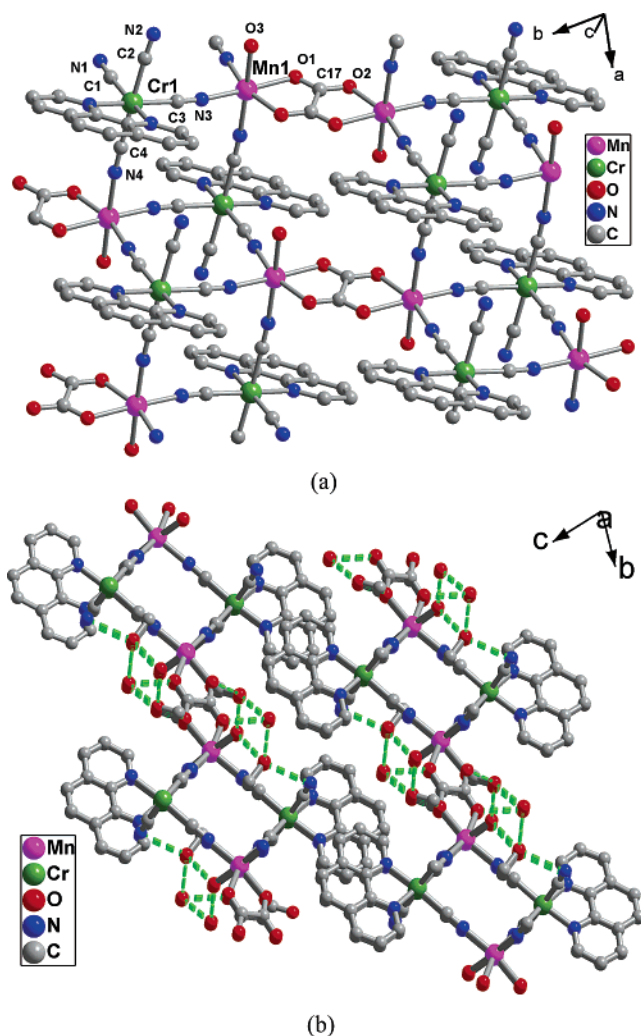


Figure 1. (a) 2D layer of **1** showing the cyano and oxalato bridges between Cr^{III} and Mn^{II} ions. (b) 3D packing view of **1** showing π - π stacking of phen \cdots phen and H bonds.

The shortest interlayer metal–metal distances ($\text{Cr}\cdots\text{Mn}$) are 9.32 Å for **1** and 9.04 Å for **2**. The lattice solvent molecules are filled in the void space between the layers, forming lots of H bonds with $\text{O}\cdots\text{O}$ distances of 2.68–2.92 Å.

Description of the Structure of 3. The structure of **3** consists of chains of $\{\text{Mn}(\text{bpy})(\mu\text{-ox})_{0.5}[\text{Cr}(\text{bpy})(\text{CN})_4]\}_n$ in which the heterometal–cyanide squares are connected by oxalato bridges. As shown in Figure 3, each $[\text{Cr}(\text{bpy})(\text{CN})_4]^-$ unit bridges two Mn^{II} ions in *cis* geometry,¹¹ and each Mn^{II} ion in turn links two $[\text{Cr}(\text{bpy})(\text{CN})_4]^-$ units in a *cis* fashion too, yielding a slightly distorted cationic square of $\{\text{Mn}(\text{bpy})[\text{Cr}(\text{bpy})(\text{CN})_4]\}_2^{2+}$ ($\angle\text{Mn}-\text{Cr}-\text{Mn}$ and $\angle\text{Cr}-\text{Mn}-\text{Cr}$ are 88.2 and 91.8°, respectively), which is similar to the backbone of compound **C**. The square size is $\sim 5.22 \times 5.40$ Å. The bridging cyano ligands coordinate to the Mn^{II} ion ($\text{Mn}-\text{N} = 2.189(4)$ and $2.224(4)$ Å) in a bent fashion with $\text{Mn}-\text{N}\equiv\text{C}$ bond angles of 152.5(4) and 165.5(4)°, respectively. Additionally, each six-coordinated Mn^{II} ion is chelated by one 2,2'-bpy ligand and further linked to the closest Mn^{II} ion from the adjacent square by one bis-bidentate oxalato

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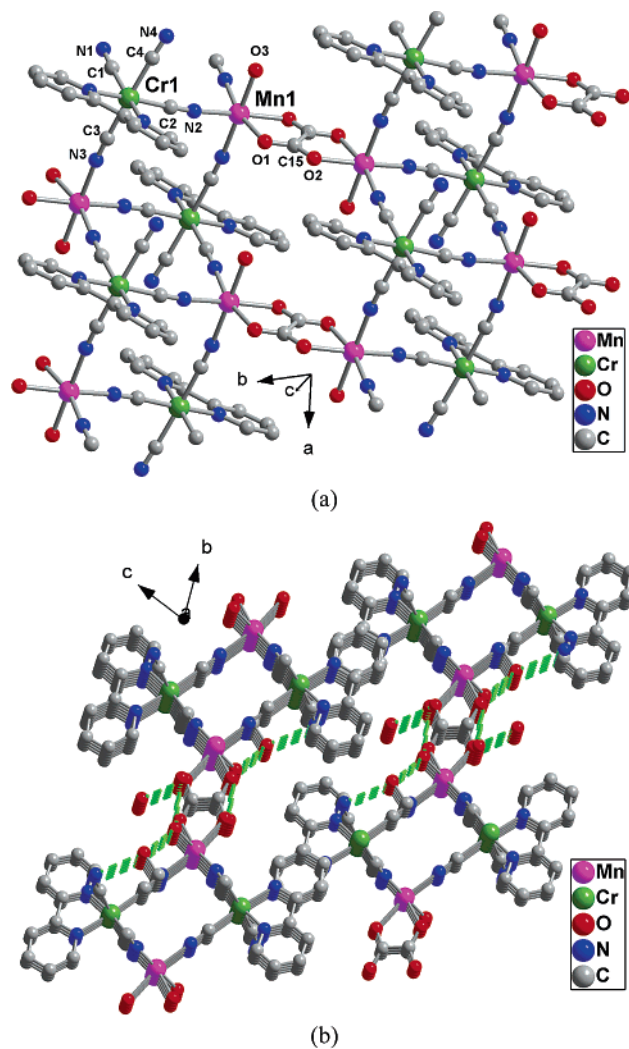


Figure 2. (a) 2D layer of **2** showing the cyano and oxalato bridges between Cr^{III} and Mn^{II} ions. (b) 3D packing view of **2** showing π - π stacking of bpy...bpy and H bonds.

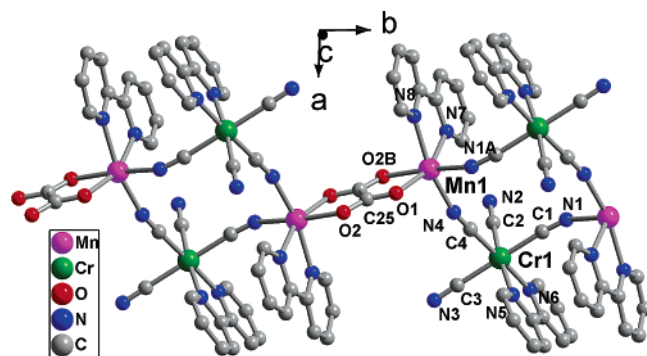


Figure 3. Chain of **3** along the *b* axis.

bridge with an Mn...Mn distance of 5.68 Å, thus forming an oxalato-bridged square-based chain. The chains run along the *b* axis, and they are roughly hexagonally packed through weak H bonds of C–H...N_{cyanoide}/O of 3.14–3.21 Å and van der Waals contacts with a shortest interchain M...M distance of 8.40 Å. (Figure S1, Supporting Information)

Synthesis and Discussion. Because oxalate is usually difficult to control in crystal engineering because of its strong chelated ability, there is an urgent need to develop some new

techniques which could provide oxalate dianions slowly and steadily. Notice that the hydrolysis reaction may occur at the C≡N bond and that the oxidation reaction may happen at the C=C double bond;^{17–19} we attempted to use DAMN as a steady oxalato provider under nonhydrothermal conditions, which is often essential for cyanide. As expected, we obtained high-quality crystals of **1** and **2**. In comparison, we also acquired them by the slow diffusion of aqueous K₂C₂O₄ into a mixed water–methanol solution of MnCl₂ and [N(CH₃)₄][Cr(L)(CN)₄] \cdot *x*H₂O after more than one month. The products from the above two methods were proven the same by element analysis, IR spectra, and single-crystal X-ray diffractions.

Here, the possible mechanism in method 1 is presumed in Scheme 1. First, Mn²⁺ ions were chelated by the amino groups of DAMN and also coordinated by the cyano groups (–CN ends); thus, the electron cloud of the ligand inclined to the Mn^{II} ions as to polarize the chemical bonds of C=C and C≡N. Then, the activated carbon centers were attacked nucleophilically by H₂O or adventitious amounts of OH[–]. As a result, the CN ends were hydrolyzed, whereas the C=C double bond was oxidation hydrolyzed, thus forming oxalate. Ulteriorly, the formation of **1** or **2** demolished the balance of the oxidation-hydrolysis reaction and promoted the transformation of DAMN to oxalate.

Further investigation of the mechanism, such as efforts to obtain the possible isomorphous compounds by the reaction with Zn^{II} in place of Mn^{II} to explore the influence of metallic ions on the reaction or studying the feasible reaction of Mn^{II}, 2,2′-bpy, and DAMN, is still under way in our lab. Anyway, the transformation of DAMN to oxalate provides useful information for employing oxalato-bridged compounds through an in situ metal-mediated oxidation-hydrolysis reaction.

Comparing azide with oxalate in this system, we found that (1) the structure of **1** is similar to that of **A**, and the π - π stacking from the middle phenyl cycles of phen might play an important role in stabilizing the structures; (2) azide could only act as terminal ligands in **B** and **C**, resulting in cyano-bridged ladderlike and squarelike structures, respectively, while oxalate could connect the ladders or squares into an extended 2D layer (**2**) or 1D chain (**3**), and especially, π - π stackings from bpy...bpy are well-formed in **2**. Hereby, whether the azide ion acts as a terminal or a bridge ligand in this system seems to depend on the given molecular interaction in the structures, whereas the oxalate dianion can facilitate the formation of extended structures as a rigid bidentate bridging ligand in all relative compounds and promote some relevant intermolecular interactions to the cohesion of the structures. This would be important to prepare hybrid materials with novel structures and special properties, especially for the synthesis of highly stable, infinite frameworks.

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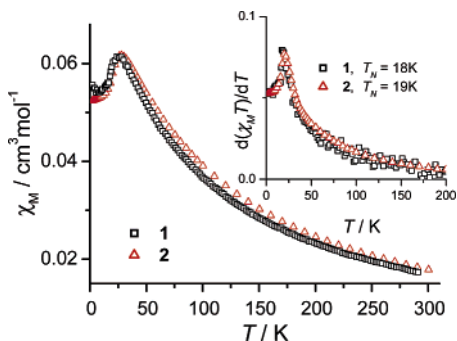


Figure 4. χ_M vs T in an applied field of 10 kOe for **1** and 2 kOe for **2**. Inset: $d(\chi_M T)/dT$ vs T curves.

Magnetic Studies. Magnetic Properties of 1 and 2. As shown in Figure 4, the magnetic susceptibilities of **1** and **2** (per [MnCr] unit) above 50 K obey the Curie–Weiss law [$\chi_M = C/(T - \theta)$] and give the Weiss (θ /K) and Curie constants ($C/\text{cm}^3 \text{mol}^{-1} \text{K}$) $\theta = -72$ and -70 and $C = 6.3$ and 6.5 for **1** and **2**, respectively. The C values are well-consistent with the spin-only value of $6.25 \text{ cm}^3 \text{mol}^{-1} \text{K}$ for the isolated $\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}$ unit ($g = 2$), and the negative θ indicates antiferromagnetic (AF) interactions between the metallic ions. The χ_M values for both **1** and **2** show round maxima at ca. 24 and 26 K, respectively, suggesting possible antiferromagnetic ordering. The increase of χ_M for **1** below 5 K might be due to paramagnetic impurities. The Néel temperatures T_N of **1** and **2** were determined from the sharp peak of $d(\chi_M T)/dT$ at 18 and 20 K, respectively, shown in the inset of Figure 4. The slightly higher T_N of **2** may be related to the shorter interlayer distance. It is well-documented that the ordering temperature of a 3D anti-ferromagnet is slightly lower than $T(\chi_{\text{max}})$,²⁰ thus, the 2D characteristics of **1** and **2** are suggested by the low ratio of $T_N/T(\chi_{\text{max}})$, 0.75 and 0.77 for **1** and **2**, respectively.

The field-dependent magnetizations $M(H)$ at 1.8 K (Figure 5a, for **1**) or 1.9 K (Figure 5b, for **2**) show a pronounced spin-flop behavior: M first increases slowly and linearly with an increase of the field because of AF ordering and then shows a spin-flop transition at a critical field (H_{sp}) of 19 kOe for **1** and 20 kOe for **2**, which was estimated from the sharp peaks of the ac susceptibility χ' (inset of Figure 5a) and dM/dH (inset of Figure 5b), respectively. At higher fields, M increases linearly again with an increase of H and reaches about $1.0 N\beta$ at 70 kOe for **1** and $0.7 N\beta$ at 50 kOe for **2**, far below the expected value of $2.0 N\beta$ for a ferrimagnetic state with $S_T = 5/2 - 3/2 = 1$ for the [MnCr] unit, confirming an AF ground state again.

Detailed field-cooled magnetization measurements (FCMs) at different fields for **1** and **2** have also been investigated (Figure 6). At lower fields, the FCM curves were almost overlapped and only round peaks at about 25 K were observed. This is consistent with the AF ordering behavior. When the applied fields were increased above ca. 20 kOe, the magnetic susceptibilities at different fields greatly diverged below ca. 20 K, further evidencing the spin-flop behavior.

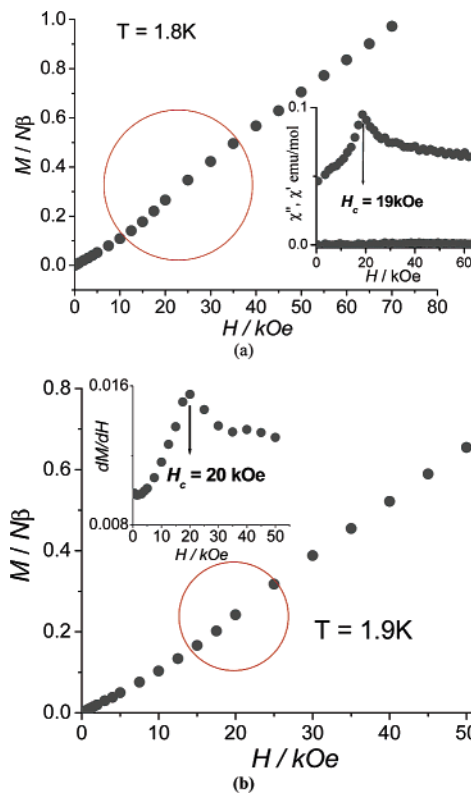


Figure 5. Field-dependent magnetizations for **1** at 1.8 K (a) and for **2** at 1.9 K (b). Inset: Field-dependent ac susceptibilities at 1.8 K for **1** and dM/dH vs H plot for **2**.

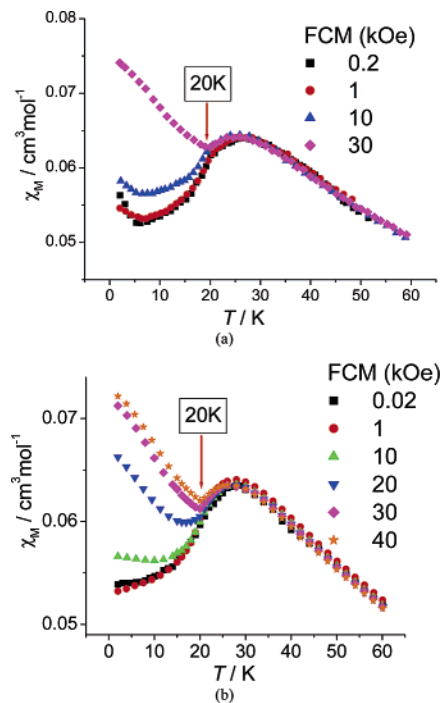
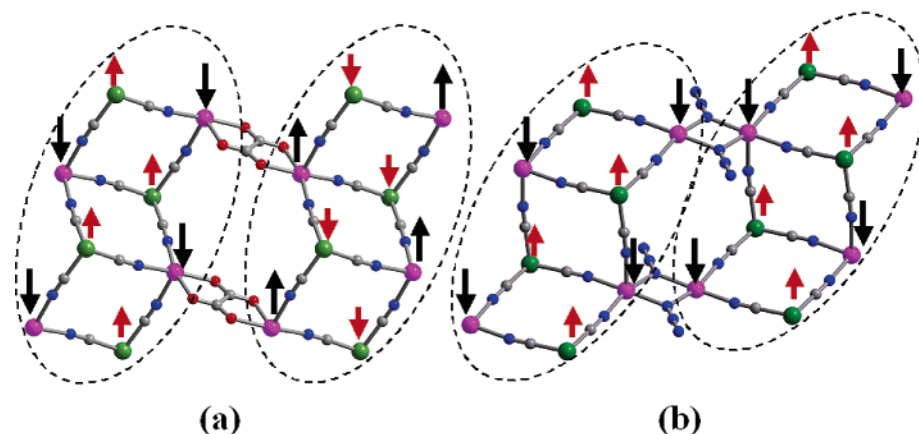


Figure 6. χ_M vs T plots for **1** (a) and **2** (b) at different fields.

The magnetic behaviors of **1** and **2** can be rationalized on the basis of their molecular structures. The oxalate dianion is well-known to mediate an AF interaction when it bridges two identical paramagnetic ions in the bis-bidentate geometry. Therefore, although Mn^{II} and Cr^{III} are AF-coupled through CN^- bridges, forming similar ferrimagnetic ladders

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Scheme 2



in **1** and **2** as well as that in the azido-bridged compound **A**, different bridges between ladders result in an extended ferrimagnetic layer by ferrimagnetic interladder interactions through azido bridges for **A** (Scheme 2b), while an AF 2D layered network forms by AF interladder interactions through ox bridges for **1** and **2** (Scheme 2a). It is found that spin-flop behavior often occurs in some antiferromagnets with weak magnetic anisotropy (Mn^{II} for example).²¹ This is just the case for the present compounds **1** and **2**.

Magnetic Properties of 3. The susceptibility (χ_M) for **3** (per [MnCr] unit) also exhibits a round maximum at about 28 K followed by a sharp increase below 10 K (Figure 7). The curve is characteristic of strong AF coupling in the 1D chain. This is supported by the value of the Weiss constant $\theta = -50$ K, obtained from fitting the magnetic data in the range of 70–300 K to the Curie–Weiss law. The Curie constant C is $6.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. The increase of χ_M below 10 K might be due to paramagnetic impurities. The magnetization value of $0.7 N\beta$ at 50 kOe at 1.8 K is greatly lower than the expected value of $2 N\beta$ for the ferrimagnetic state for [MnCr] with $S_T = 5/2 - 3/2 = 1$ (inset of Figure 7).

On the basis of the empirical relationship between the coupling constant (J) and the Mn–N≡C angle (θ),¹¹ the AF coupling constant (J_1) through the Mn–N≡C–Cr bridges in **3** [$\angle\text{Mn–N–C} = 152.5(4)$ and $165.5(4)^\circ$] could be estimated in the range of -7 to -9 cm^{-1} . It would be obviously larger than that between high-spin Mn^{II} ions

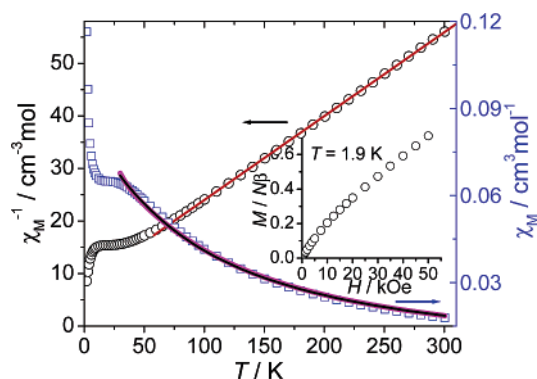
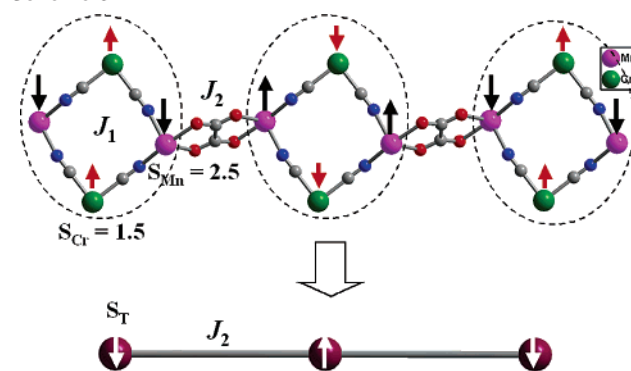


Figure 7. χ_M and $1/\chi_M$ vs T in an applied field of 10 kOe for **3**. The solid lines correspond to the best fit to the Curie–Weiss law, an approximate uniform-chain model, and a square tetranuclear model. Inset: M vs H plot at 1.9 K.

Scheme 3



through bis-bidentate oxalato-bridges (J_2) and was analyzed at a value of about -1 cm^{-1} for $d(\text{Mn}\cdots\text{Mn}) = 5.7 \text{ \AA}$.^{13–15} Thus, the magnetic chain of **3** can be viewed as Scheme 3 on the basis of an approximate model,^{4e,22} where the square tetranuclear $[\text{Cr}_2\text{Mn}_2]$ was treated as the repeat unit of a uniform chain: $H = -J_1(S_{\text{Cr}1}S_{\text{Mn}1} + S_{\text{Mn}1}S_{\text{Cr}2} + S_{\text{Cr}2}S_{\text{Mn}2} + S_{\text{Mn}2}S_{\text{Cr}1})$ (for the square $[\text{Cr}_2\text{Mn}_2]$); $H = -J_2\sum S_{T,i}S_{T,i+1}$ (S_T for $[\text{Cr}_2\text{Mn}_2]$ as a classical system). J_1 and J_2 were found to be strongly correlative. Nevertheless, the best fitting of the data in the range 30–300 K with fixing $J_1 = -6.9 \text{ cm}^{-1}$ gives $g = 2.05$, $J_2 = -0.8 \text{ cm}^{-1}$, and $R = 4.1 \times 10^{-4}$. If fixing $J_2 = -1.0 \text{ cm}^{-1}$, it gives $g = 2.05$, $J_1 = -5.9 \text{ cm}^{-1}$, and $R = 3.4 \times 10^{-4}$ [$R = \sum [(\chi_M T)_{\text{obs}} - (\chi_M T)_{\text{calcd}}]^2 / \sum (\chi_M T)_{\text{obs}}^2$]. For a comparison, another approach was executed, where an isolated square tetranuclear $[\text{Cr}_2\text{Mn}_2]$ model was used, and both J_2 and the interchain interactions were treated as intermolecular interactions (zJ') by mean field theory, giving the best fitting: $J_1 = -6.1 \text{ cm}^{-1}$, $zJ' = -1.2 \text{ cm}^{-1}$, $g = 2.07$, and $R = 4.3 \times 10^{-4}$. Thus, all of the results were well-consistent and confirmed the AF couplings between cyano-bridged Cr^{III}–Mn^{II} and oxalato-bridged Mn^{II}–Mn^{II} ions.

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Conclusion

In this paper, on the basis of versatile cyanide building blocks $[\text{Cr}(\text{L})(\text{CN})_4]^-$, we have succeeded in combining cyanide and oxalate bridges to synthesize three novel heterometallic Cr–Mn compounds (**1–3**), where cyano-bridged corrugated ladderlike chains or squares are further connected through bis-bidentate oxalato bridges to unique 2D layered compounds (**1** and **2**) or a chainlike compound (**3**). To the best of our knowledge, compounds **1–3** represent the first molecular magnetic materials containing cyanide and oxalate bridges. We also demonstrated that DAMN could act as one convenient oxalate precursor and might breed an interesting route to employ new oxalato-bridged compounds through an in situ metal-mediated oxidation-hydrolysis reaction. Magnetic studies showed that the coupling between cyano-bridged Cr–Mn and oxalato-bridged Mn(II) ions are AF in character. The 2D AF layered compounds exhibit spin-flop behaviors below their Neél temperature of 18 K for **1** and 19 K for **2**. Compared with azide, the oxalate dianion is

superior in preparing hybrid materials with novel and extended structures, especially for synthesizing highly stable, infinite frameworks. Further investigations on the mechanism of the oxidation-hydrolysis reaction of DAMN and combining cyanide with other effective bridges are under way.

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Supporting Information Available: CIF files of the crystal structures of complexes **1–3** and a packing plot and XRD patterns for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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