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Cyanide-Bridged W(V)–Mn(II) Bimetallic Double-Zigzag Chains with a Metamagnetic Nature

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A cyanide-bridged W–Mn bimetallic compound $[W(CN)_6(bpy)]_2[Mn(H_2O)_2]\cdot 4H_2O$ (**1**) (bpy = 2,2′-bipyridine) with a one-dimensional, crossed double-zigzag chain structure was prepared by self-assembling $[W(CN)_6(bpy)]^-$ and Mn^{2+} ions in a 2:1 reaction ratio. The magnetic properties of **1** exhibit a field-induced metamagnetic behavior.

Cyanide-bridged molecule-based magnetic materials with reduced dimensionality, such as single-molecule magnets and single-chain magnets, have attracted intensive attention owing to their potential applications to information storage.[1] One synthetic approach to attain discrete or one-dimensional (1D) systems is to utilize molecular precursors with ample coordinating capability, for instance, $[M(CN)_p]^{n-}$ ($p = 6, 8$), and their counterparts having specific vacant sites or labile leaving ligands, $[M'L_xL'_y]^{m+}$ (L = polydentate ligand, L′ = labile group).[2] In this situation, the denticity of the polydentate ligand becomes a determining factor for molecular dimensionality. Recently, a more efficient strategy in which capped cyanide-coordinated building units $[M(CN)_pL_q]^{n-}$ (M = Cr^{III}, Fe^{III}, Mo^{III}, Re^{II}) can be employed as synthons to achieve low-dimensional magnetic complexes has been successfully devised.[3–6] The building blocks containing the 3d metal ions have been extensively explored, giving diverse structural motifs spanning from clusters, 1D chains, to 2D sheets.[3,4,7,8] In contrast, low-dimensional materials with the 4d or 5d transition-metal ions have also been studied, but examples of such compounds are still scarce to date, although the 4d or 5d magnetic orbitals are expected to interact strongly through bridging ligands compared to the 3d magnetic orbitals.[5,6] Additionally, reported cyanide-bridged bimetallic magnetic assemblies have been known to possess the number of p in $[M(CN)_pL_q]^{n-}$ only up to 4.[3–8] In this vein, for the first time, we have attempted to utilize $[W(CN)_6(bpy)]^-$, notably including $p = 6$, as a new appropriate magnetic building brick to fabricate magnetically interesting low-dimensional systems. Herein we report a new cyanide-linked compound of a 1D system $[W(CN)_6(bpy)]_2[Mn(H_2O)_2]\cdot 4H_2O$ (**1**) with double-zigzag chains, marking the first example of the cyanide-bridged bimetallic complexes, which comprises the capped molecular building block with the paramagnetic 5d metal ion and six CN groups. **1** shows a ferrimagnetic nature within a chain, leading to a metamagnet.

$(AsPh_4)[W(CN)_6(bpy)]$[9] (0.056 mmol) in MeCN was slowly added to $Mn(ClO_4)_2\cdot 6H_2O$ (0.028 mmol) in H_2O. The resulting red solution was filtered and left undisturbed in the dark. After several days, the filtrate gave red crystals of **1** in a yield of 34%.[10] It is noted that a reaction ratio of

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(10) Anal. Calcd for **1**: C, 33.21; H, 2.61; N, 19.36. Found: C, 32.91; H, 2.32; N, 18.87. Crystal data for **1**: $C_{16}H_{14}Mn_{0.5}N_8O_3W$, fw = 577.67, triclinic, space group $P\bar{1}$, $a = 8.4715(12)$ Å, $b = 10.5250(15)$ Å, $c = 11.9813(16)$ Å, $\alpha = 99.290(4)°$, $\beta = 100.791(4)°$, $\gamma = 107.102(4)°$, $V = 976.0(2)$ Å^3, $Z = 2$, $D_{calc} = 1.966$ g cm^{-3}, 12 476 reflections collected, 4525 unique ($R_{int} = 0.0434$), R1 = 0.0634, wR2 = 0.1839 [$I > 2\sigma(I)$].

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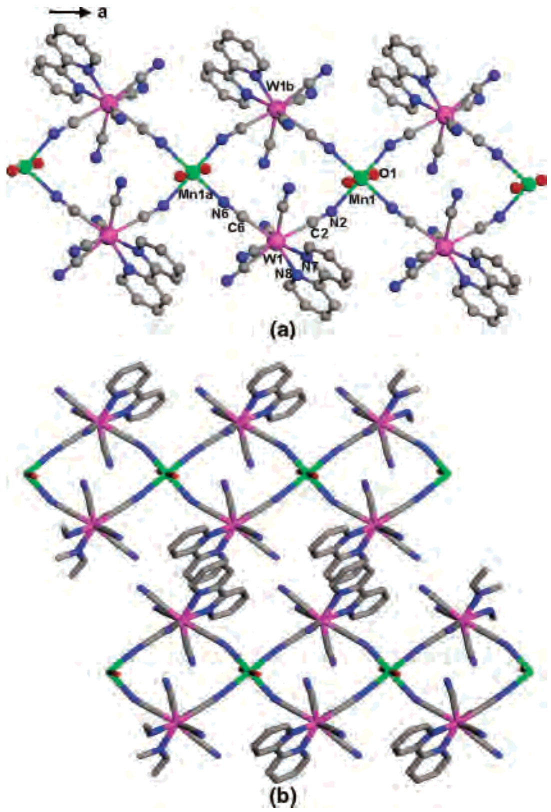

Figure 1. (a) Molecular view of **1**. Symmetry code: $a = -1 + x, y, z$ and $b = 1 - x, -y, -z$. (b) Extended structure of **1** showing $\pi-\pi$ interactions between pyridyl rings of bpy ligands. Colors present W in pink, Mn in green, N in blue, O in red, and C in gray.

$[W(CN)_6(bpy)]^-$:Mn^{2+} = 2:1 afforded **1**, while a 1:1 ratio produced $[W(CN)_6(bpy)][Mn(H_2O)_3]\cdot 4.5H_2O$ (**2**) in a low yield of 7%.[11] It is evident that the W ion in **2** is reduced from W(V) to W(IV), supported by the IR and crystal structure. The reduction mechanism remains elusive for the moment,[12] but the ratio of the reactants seems to play a role. The IR data for **1** show peaks centered at 2185m, 2165w, 2156vw, and 2148vw cm^{-1}. Among them, the band observed at 2185 cm^{-1} can be assigned to bridging CN groups, and the remaining are attributable to terminal CN groups in comparison with the IR peaks of the precursor present at 2160w, 2151vw, 2144vw, 2134vw, 2124vw cm^{-1}.

Figure 1a displays the neutral double-zigzag W(V)−Mn(II) chains of **1** running along the *a* axis whose structural motif is also found in $[Fe^{III}(CN)_4L]_2[M^{II}(H_2O)_2]\cdot 4H_2O$ [L = bpy, 1,10-phenanthroline (phen); M = Mn, Co, Zn] and $[Cr^{III}(CN)_4L]_2[Mn^{II}(H_2O)_2]\cdot 4H_2O$.[3,4] The W(V) atom in a distorted square antiprismatic geometry is coordinated by six CN groups and one bpy ligand [$W-C_{av}$ = 2.138(9) Å, $W-N_{av}$ = 2.236(1) Å]. The average W−CN angle is almost linear, 176.7(14)°, consistent with those found in octacyanotungstate-based bimetallic complexes.[13] The $[W(CN)_6(bpy)]^-$ moiety is linked in cis mode to two Mn^{II} ions in octahedral arrangements, forming a four-membered macrocyclic entity [W1−Mn1 = 5.322(1) Å, W1−Mn1a = 5.480(1) Å, W1−W1b = 6.704(1) Å, Mn1−Mn1a = 8.472(1) Å]. The Mn−NC angles are 145.6(10)° for Mn1−N2−C2 and 170.8(12)° for Mn1a−N6−C6, which are significantly deviated from linearity. Noncovalent forces of $\pi-\pi$ contacts between pyridyl rings of bpy ligands in adjacent chains are operative in the range of 3.902−4.205 Å (Figure 1b), and hydrogen bonds are established among coordinated and lattice water molecules and terminal CN groups, generating a 3D framework (Figure S1 in the Supporting Information). The shortest interchain distances of W−W, W−Mn, and Mn−Mn are 7.620(1), 9.363(1), and 10.525(2) Å, respectively.

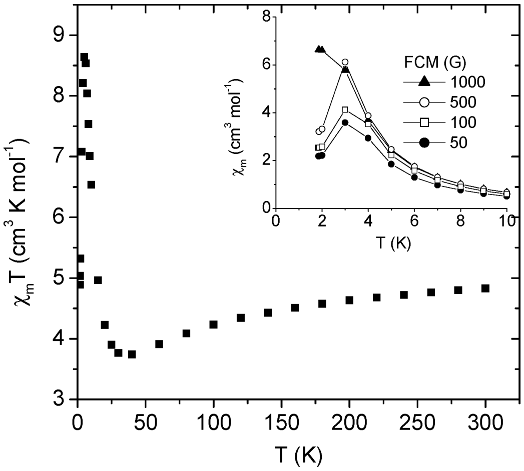

Figure 2. Plot of $\chi_m T$ vs T at 0.5 T for **1**. The inset, in which the solid lines are guides, presents the temperature dependence of the field-cooled magnetization (FCM) at various fields.

The thermal variation of $\chi_m T$ per $W^V{}_2Mn^{II}$ unit of **1** is shown in Figure 2. The $\chi_m T$ value of 4.828 cm^3 K mol^{-1} at 300 K is slightly smaller than the spin-only one (5.125 cm^3 K mol^{-1}) expected for two isolated W(V) and one Mn(II) centers. The monotonic decrease in $\chi_m T$ on cooling proceeds until a minimum at 40 K is reached. The occurrence of the minimum in $\chi_m T$ at T_{min} = 40 K indicates short-range antiferromagnetic couplings between W(V) ($S_W = {}^1/_2$) and Mn(II) ($S_{Mn} = {}^5/_2$) magnetic centers within a chain, with the noncompensation of the spins with different spin multiplicities eventually displaying such a ferrimagnetic nature. When compared with $[Fe(CN)_4L]_2[Mn(H_2O)_2]$ (L = bpy, phen) chains in which a minimum in $\chi_m T$ is found at 12 K for L = phen and is not observed for L = bpy, the higher minimum temperature of 40 K in **1** suggests that the strength of magnetic interactions between W(V) ($S_W = {}^1/_2$) and Mn(II) ($S_{Mn} = {}^5/_2$) is stronger than that for the Fe(III) ($S_{Fe} = {}^1/_2$)−Mn(II) ($S_{Mn} = {}^5/_2$) pair possibly because of the fact that the 5d orbital on W(V) is more diffuse than the 3d orbital on Fe(III).[4a,13,14] Below T_{min}, $\chi_m T$ goes on a sharp rise up to 8.640 cm^3 K mol^{-1} at 5 K because of the extended correlation length through a chain. At T < 5 K, $\chi_m T$ experiences an abrupt drop, which appears to arise from antiferromagnetic arrangements between the ferrimagnetic chains. In the high-

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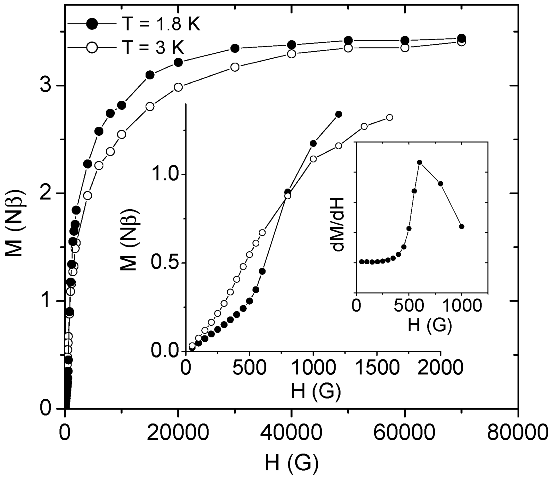

Figure 3. Field dependence of the magnetization of **1** at 1.8 and 3 K. The insets indicate the blowup of *M*(*H*) in the low-field regime and the plot of d*M*/d*H* vs *H* at 1.8 K. The solid lines are guides.

temperature range of 60−300 K, the magnetic data obey the Curie−Weiss equation [$\chi_m = C/(T - \theta)$], affording $C = 5.150$ cm^3 K mol^{-1} and $\theta = -21.5$ K (Figure S2 in the Supporting Information). The negative value of θ ensures that neighboring spins of W(V) and Mn(II) ions are coupled antiferromagnetically.

The field-dependent magnetization at 1.8 K, illustrated in Figure 3, displays an explicit sigmoidal curve. An inflection point is present at $H_C = 600$ G from the peak position of d*M*/d*T* in the inset of Figure 3. At $H < 600$ G, a linear increase in *M*(*H*) is associated with antiferromagnetic interactions, and then above the critical field, the magnetization is drastically increased and saturated to a value of 3.4 Nβ at 7 T, almost consistent with a ferrimagnetic phase ($S_T = {}^5/_2 - 1 = {}^3/_2$ for a $W^V{}_2Mn^{II}$ unit). This behavior is typical of a metamagnet,[3] which is confirmed by the χ_m vs *T* plots at various fields in the inset of Figure 2. In $\chi_m(T)$ below 600 G, the observation of peaks at 3 K is a signature of the existence of antiferromagnetic interactions between chains, while the lack of the peak at $H > 600$ G implies a field-induced magnetic phase transition to the ferrimagnetic state.

A magnetic model accounts for the observed ferrimagnetic behavior characterized by the temperature and field dependencies of the magnetization. The exchange coupling for the system can be written as $J = (1/n_An_B)\sum_{\mu}^{n_A}\sum_{\nu}^{n_B}J_{\mu\nu}$, where the total exchange coupling constant (*J*) consists of the antiferromagnetic component (J_{AF}) and ferromagnetic contribution (J_F).[15] The magnetic d_{z^2} orbital on W(V) can be delocalized over the π orbital of the CN bridge in a π pathway, which matches well in symmetry with d_π orbitals on Mn(II), so that dominant antiferromagnetic interactions ($J_{AF} > J_F$) become realized and facilitate the overall ferrimagnetic feature among W(V) and Mn(II) spins in a chain.[12] There is no proper theoretical expression to analyze the magnetic properties of **1**, as is also observed in the case of $Fe^{III}{}_2Mn$ double-zigzag chains containing $S_{Fe} = {}^1/_2$ and $S_{Mn} = {}^5/_2$.[4a]

In summary, we have characterized a new W−Mn bimetallic coordination polymer by employing a stoichiometric ratio of $[W(CN)_6(bpy)]^-:Mn^{2+} = 2:1$. **1** shows a double-zigzag chain structure and functions as a metamagnet. The new molecular precursor $[W(CN)_6(bpy)]^-$ could be used to construct novel molecule-based magnetic materials such as single-molecule and single-chain magnets.

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Supporting Information Available: Extended structure and magnetic data for **1** (Figures S1 and S2). X-ray crystallographic file for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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