INTRODUCTION

In the past few years, the design and synthesis of coordination compounds have attracted much attention because of their intriguing topologies and fascinating potential applications. Especially, considerable efforts into crystal engineering have been devoted to the design and construction of octacyanometallates \([M(CN)_{8}]^-\) as carriers of unpaired spin with 3d metal ions has produced various dimensional molecular magnets. Octacyanometallates as versatile building blocks have been usually used to control the coordination number and spatial arrangement around metal centers for cyanide-bridging, thus resulting in low-dimensional octacyanometallate-based structures rather than extended frameworks, while longer bridging ligands (e.g., polypyridines, pyridyl N-oxides) were used to construct high-dimensional structures. Notably, spacer ligands have been applied in the construction of extended networks from preorganized \(M_nW_6\) clusters; for example, \(\{MnW_6\}\) clusters could be connected by 4,4′-bipyridine (4,4′-bpy) and trans-1,2-di(4-pyridyl)ethene (dpe) linkers into 2D and 3D hybrid networks, respectively. Meanwhile, \(\{Co_3W_6\}\) clusters were combined with 4,4′-bipyridine-N,N′-dioxide (4,4′-bdpo) linkers, forming H-bonded supramolecular chains and 1D nanowires. However, how to control rationally the desired structures with specific properties still remains a great challenge. In order to search for effective synthetic strategies of high-dimensional octacyanometallate-based compounds, and then further investigate the structure-magnetism correlations involved in such systems, the in situ and secondary assembly methods were employed recently by our group in the presence of linear bridging ligands dpe and 4,4′-azopyridine (azpy), isolating three manganese(II)-octacyanotungstate(V) bimetallic compounds with 1D or 3D structures: \(\{Mn(H_2O)_2(dpe)\}_3[W(CN)_8]_2\cdot2dpe\cdot7H_2O\) (1), \(\{Mn(H_2O)_2(azpy)\}_3[W(CN)_8]_2\cdot7H_2O\) (2), and \(\{Mn(CH_2CN)_2(azpy)\}_3[W(CN)_8]_2\cdot2azpy\cdot2H_2O\) (3) were prepared by in situ or secondary assembly methods. Compounds 1 and 2 show three-dimensional (3D) networks through the cross-link of one-dimensional (1D) infinite 3,2-chains or rope-ladder chains with linear ligands (dpe, azpy), while compound 3 adopts a 1D ribbon-like structure by the connection of pentanuclear repeating units with azpy linkers. Magnetic studies reveal that compounds 1–3 show intramolecular antiferromagnetic coupling between Mn(II) and W(V) centers, which produce the typical ferrimagnetic chain behaviors for compounds 1 and 2 but paramagnetic properties for compound 3. Notably, field-induced metamagnetic behavior was detected for compound 2, indicating it undergoes a transition from the antiferromagnetic ground state to ferrimagnetic phase above critical dc field.
Syntheses of [Mn(H₂O)₃(azpy)]·[Mn(CH₃CN)₂(azpy)]·W(CN)₈·2H₂O (3). A small glass vial (3 mL) containing diethyl ether solvent was placed into a big glass vial (15 mL) containing the solids of Mn(ClO₄)₂·6H₂O (0.075 mmol, 27.15 mg), [HN(C₆H₄)ₓ]W(CN)₈ (0.05 mmol, 40.55 mg) and azpy (0.1 mmol, 18.42 mg). Then an acetonitrile/water (V/V = 1:1) solution (8 mL) was poured slowly into the big vial until the liquid level was just below the small vial. The big vial was sealed, and block-shaped red crystals were obtained after 2 weeks at room temperature. The crystals were filtered, washed in acetonitrile/water, and dried in air. IR: v(CCN) = 2162, 2117 cm⁻¹. Anal. Calcd for C₁₀₀H₈₆Mn₃N₅₀O₈W₂ (3) (%): C, 45.35; H, 3.27; N, 26.44. Found: C, 45.79; H, 3.16; N, 26.89. Yield (based on Mn salt): ∼36%.

Crystallographic Data Collection and Structural Determination. Diffraction data for compounds 1–3 were collected on a Bruker Smart Apex II diffractometer equipped with Mo-Kα (λ = 0.71073 Å) radiation. Diffraction data analysis and reduction were performed within SMART, SAINT, and XPREP.24 Correction for Lorentz, polarization and absorption effects were performed within SADABS.25 Structures were solved using the Patterson method within SHELXS-97 and refined using SHELXL-97.23–25 All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms of dpe, azpy, and acetonitrile molecules were calculated at idealized positions and included in the refinement in a riding mode. The H atoms bound to water molecules were located from difference Fourier maps and refined as riding. The O6W–O11W atoms of water molecules in the structure of compound 1 are all disordered and have different occupancies of 0.30–0.50. The crystallographic data and structural refinement for compounds 1–3 are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The full structures of compounds 1–3 are provided in the Supporting Information (Figures S4–S6). Crystallographic data of compounds 1, 2, and 3 have been deposited at the Cambridge Crystallographic Data Centre as CCDC numbers 991486, 991487, and 991488, respectively.

**EXPERIMENTAL SECTION**

General Considerations. All chemicals and solvents were purchase from Alfa Aesar and used as received. Mn(ClO₄)₂·6H₂O, trans-1,2-di(4-pyridyl)ethene (dpe) ligand were purchased from Alfa Aesar and used without further purification. The [HN(C₆H₄)ₓ]W(CN)₈ precursor and 4,4′-azopyridine (azpy) ligand were prepared according to the published procedures.26,27 Elemental analyses for C, H, and N were performed with a PerkinElmer 240C elemental analyzer. IR spectra were measured on a Nicolet FT 1703X spectrophotometer in the form of KBr pellets from 4000 to 400 cm⁻¹. All magnetic measurements on microcrystalline sample were conducted on a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer. Corrections of measured susceptibilities were carried out considering both the sample holder as the background and the diamagnetism of the constituent atoms according to Pascal’s tables.20

Syntheses of [Mn(H₂O)₃(azpy)]·[Mn(CH₃CN)₂(azpy)]·W(CN)₈·2H₂O (2). A small glass vial (3 mL) containing diethyl ether solvent was placed into a big glass vial (15 mL) containing the solids of Mn(ClO₄)₂·6H₂O (0.075 mmol, 27.15 mg), [HN(C₆H₄)ₓ]W(CN)₈ (0.05 mmol, 40.55 mg) and azpy (0.1 mmol, 18.42 mg). Then an acetonitrile/water (V/V = 1:1) solution (8 mL) was poured slowly into the big vial until the liquid level was just below the small vial. The big vial was sealed, and block-shaped red crystals were obtained after 2 weeks at room temperature. The crystals were filtered, washed in acetonitrile/water, and dried in air. IR: v(CCN) = 2162, 2117 cm⁻¹. Anal. Calcd for C₇₆H₇₆Mn₃N₂₆O₁₃W₂ (2) (%): C, 45.35; H, 3.27; N, 26.44. Found: C, 45.79; H, 3.16; N, 26.89. Yield (based on Mn salt): ∼31%.

Results and Discussion. Syntheses. To organize MₙWₙ (M = Mn, Co) clusters into coordination assemblies, spacer ligands such as 4,4′-bpy, dpe, or 4,4′-bpdca have been employed successfully in the assembling of hybrid networks.25–27 Following this approach, we also applied this assembly method in the syntheses of our products. However, the target compounds were not obtained. When the
preorganized Mn,W6 clusters were used to react with spacer ligands (dpe, azpy), unexpectedly 3D Mn(II)−W(V) compounds 1 and 2 were isolated instead of Mn9W6-based hybrid networks. No clusters were found in the structures of both compounds. The asymmetric unit contains two octacyanotungstate units, two noncoordinated dpe ligands, and two water molecules in the arrangement, with an octahedral Mn1N3O6 geometry. The Mn1−N4 and Mn1−N11 bond distances are 2.218(6) Å from the same plane.

**Crystal Structures.** Single crystal X-ray diffraction results show that compound 1 crystallizes in the monoclinic space group C2/c and shows a 3D network through the cross-link of 1D infinite 3,2-chains with linear dpe ligands. The asymmetric unit consists of three \([\text{Mn(H}_2\text{O})_2\text{(dpe)}]^{2+}\) cations, two \([\text{W(CN)}]^{3-}\) anions, two noncoordinated dpe ligands, and seven crystallized water molecules (Figure 1). The W atom adopted a slightly distorted square antiprism geometry, in which three cyanide groups bridge to the neighboring Mn centers and the others are terminal. The W1−C and C−N bond distances range from 2.151(7) to 2.189(6) Å and from 1.128(8) to 1.182(8) Å, respectively, while all W−CN units are almost linear with the maximum deviation from linearity of 7.1°. The coordination parameters of the W center are typical of octacyanotungstates.26−29 The \([\text{Mn(H}_2\text{O})_2\text{(dpe)}]^{2+}\) moiety is comprised two independent Mn centers (Mn1 and Mn2). The Mn1 atom is six-coordinated by two trans dpe ligands, two trans bridged CN groups, and two water molecules in the \textit{trans} arrangement, with an octahedral \([\text{MnN}_3\text{O}_6]^{2-}\) geometry. The Mn1−N4 and Mn1−N11 bond distances are 2.209(6) and 2.241(5) Å, respectively, and the Mn1−O1W bond length is 2.211(4) Å. The coordinated geometry around the Mn2 center is different from that around Mn1. Two water molecules coordinated to Mn2 atom in the octahedral \([\text{Mn}_2\text{N}_2\text{O}_7]^{2-}\) unit exhibits the cis arrangement. Furthermore, the dihedral angle of two aromatic rings from dpe ligand coordinated to Mn2 atom is about 24.25°, while two rings observed in Mn1 center are in the same plane.

As shown in Figure 2, the W1 and Mn2 centers are connected alternatively by cyanide bridges to generate a four-
metallic 12-atom rhombic ring, $\mathrm{Mn}_3\mathrm{W}_2\mathrm{(CN)}_4$ (Figure 2), where $\mathrm{W}1$ and $\mathrm{Mn}2$ atoms are located on the vertexes, while cyanide groups form the sides. The diagonal dimensions of the rhombus are approximately 8.335 Å ($\mathrm{W}1$−$\mathrm{Mn}2$), 12.623 and 13.825 Å, respectively, while the $\mathrm{Mn}1$ distances in the chain is about 16.350 Å. The 3,2-chain structure has also been documented in related cyanide-based systems.34,35

As a result, the chains are further cross-linked by dpe ligands running along two different directions (33.911° of torsion angle), generating a 3D network (Figure 3), in which noncoordinated dpe ligands and crystallized water molecules are trapped. It should be noted here that the 3,2-chains in compound $\mathrm{Cu}_{n}$ are trapped. It should be noted here that the 3,2-chains in compound $\mathrm{Cu}^+\left(\mu-4,4'-\text{bpy}\right)\left(\text{DMF}\right)_{2}\left[\mathrm{Cu}^+\left(\mu-4,4'-\text{bpy}\right)\left(\text{DMF}\right)_{2}\left[\mathrm{W}(\text{CN})_8\right]_{2}\text{DMF}2\text{H}_2\text{O}$ are linked by 4,4’-bpy along the same $[0\ 0\ 1]$ direction, forming a 2D grid layer.36

The structural difference between both compounds may be reasonably attributed to distinct connection directions of linear ligands. Terminal cyanide ligands, coordinated and uncoordinated water molecules, and crystallized dpe ligands are all involved in the formation of the hydrogen-bonding network. Uncoordinated water molecules interact with terminal cyanide ligands through O−H⋯N hydrogen bonds, while the coordinated water molecules interact with uncoordinated water by O−H⋯O hydrogen bonds. Simultaneously, the coordinated water molecules interact with uncoordinated dpe ligands through the O−H⋯N hydrogen bonds.
Compound 3 crystallizes in the monoclinic space group $P_{21}/c$ and adopts a 1D ribbon structure by the connection of pentanuclear repeating units with azpy linkers. To the best of our knowledge, the ribbon-like structure observed in our case has not been documented in octacyanometallate-based system so far. The asymmetrical unit contains two $\text{[Mn-(H}_2\text{O})_3(\text{azpy})]^2+\text{} cations, one }\text{[Mn(CH}_3\text{CN})_2(\text{azpy})]^3+\text{ cation, two }\text{[W(CN)}_8\text{]}^{3-}\text{ anions, five noncoordinated azpy ligands, and two crystallized water molecules (Figure 7).}

The geometry of the W atom surrounded by eight CN ligands is determined as a distorted square antiprism. Two trans cyanide groups bridged to two adjacent Mn centers, and the others are terminal. Both the crystallographically independent Mn1 and Mn2 atoms take a distorted slightly octahedral configuration. The coordinated sites of Mn1 atom are filled by one cyanide group, two trans azpy ligands, and three water molecules, while Mn2 atom is occupied by two cyanide groups, two trans azpy ligands, and two CH$_3$CN molecules. As shown in Figure 8, the Mn and W atoms are linked alternatively through cyanide bridges to form a pentanuclear repeating unit with the length of 20.598 Å (Mn1···Mn1 distance). Thus, the adjacent chains are further connected along the $a$ axis by trans azpy ligands to generate a ribbon-like structure (Figure 9). The lattice water molecules and noncoordinated azpy ligands are filled between the ribbons. In the network of compound 3, coordinated water molecules interact with terminal cyanide ligands or uncoordinated azpy ligands through O−H···N hydrogen bonds. Furthermore, the uncoordinated water molecules also interact with terminal cyanide groups through...
the O–H···N hydrogen bonds. The distance of neighboring ribbons is equal to 13.635 Å (Mn1···Mn1 distance).

**Magnetic Properties.** The measurements of variable-temperature magnetic susceptibilities were performed on polycrystalline samples of compounds 1–3 from 1.8 to 300 K in a typical applied field of 2 kOe. Because of the metamagnetic-like properties of compound 2, further measurement of the susceptibility data of compound 2 was carried out (1.8–15 K) in various applied dc fields ranging from 2 kOe to 0.2 kOe. For compound 2, the susceptibility measured at high field (higher than 1 kOe) might prevent the metamagnetic magnetic phase transition at very low temperature, but this influence could be safely neglected in a high temperature region. So, all the data of compounds 1–3 collected in 2 kOe were plotted for general discussion. As shown in Figure 10a,c,e, the $\chi_M T$ values (per Mn$^{III}$W$^{V}_2$) of compounds 1–3 at room temperature are 12.63, 14.49, and 12.88 cm$^3$ K mol$^{-1}$, respectively, which are overall consistent with the spin-only value of 13.87 cm$^3$ K mol$^{-1}$ calculated for the Mn$^{III}$W$^{V}_2$ unit.
SW = 1/2, SMn = 5/2) assuming gW = gMn = 2.0. As revealed by previous studied WV−CN−MnII systems,36−44 antiferromagnetic interactions between WV and MnII ions are always observed, and thus the room temperature χM T values are often slightly smaller than spin-only ones.

Upon cooling, the χM T value of compound 1 keeps almost constant, while that for compound 2 decreases gradually. But as the system further cools down, an abruptly increase of the χM T values was observed with the values changing from 12.77 to 115.26 cm3 K mol−1 for compound 1 and 12.25 to 91.48 cm3 K mol−1 for compound 2, respectively. Such behaviors are obviously an indication of the long-range magnetic ordering resulting from the interaction between WV and MnII ions. Finally, the χM T values of compounds 1 and 2 again decrease until they reach 54.20 and 48.54 cm3 K mol−1 at 1.8 K. No maximum was detected in the χM vs T curve measured at 2 kOe (inset of Figure 10a,c), the downturn of the values at very low temperature could be ascribed to the saturation effect and/or intermolecular antiferromagnetic interactions. The χM T vs T curve of compound 3 shows mainly a comparable feature to compounds 1 and 2, but no abruptly increase of the χM T values was observed at the low temperature region. The Curie−Weiss fitting for compounds 1−3 between 100 and 300 K gives the Weiss constants of 1.2(4) K, −27.1(22) K, and −6.2(5) K, respectively. It is still insufficient to claim that the intramolecular WV⋯MnII interactions are antiferromagnetic (AF). However, associated with the ferrimagnetic properties of other cyanide bridged WV⋯MnII compounds with extended structures,45,46 the negative Weiss constants might be an indication of the antiferromagnetic WV⋯MnII interactions presented in compounds 2 and 3. The very small positive Weiss constant of compound 1 observed should be taken with caution because it is contradictory to the well-known AF nature of WV⋯MnV interactions. Such unconventional phenomena were also observed in the literature,15,16,45,47 and one reasonable explanation is that the large diffusion of the 4d and 5d orbital leads to coupling interaction in a wide range of temperature, and thus the minimum of the χM T curve for antiferromagnetically coupled WV and MnII ions might become very broad or even at higher temperatures than room temperature.

To the best of our knowledge, no available suitable theoretical models could be used for evaluating quantitatively the magnitude and sign of the magnetic coupling constants in such complicated systems of compounds 1−3. However, the magnetostructural correlations could be qualitatively described. From the structural analysis result, compounds 1 and 2 show such peculiar 3D topological structures. Actually, the structures could be simplified as 1D Mn−W chains that are tied together by the organic ligands. From the magnetic point of view, the magnetic exchanges mediated by the CN bridges would be much stronger than that for organic ligands pathways because the latter produce very long separations between the spin carriers. On the basis of the above assumptions, the χM T vs T behaviors of compounds 1 and 2 are actually governed by the ferrimagnetic Mn−W chains, while compound 3 is simply 0D spin clusters. Therefore, the decreases of the χM T at the high temperature region are a unanimously short-range order state where the spins of adjacent Mn and W are antiparallel arranged. As the temperature further decreases, the correlation length

Figure 11. Variable-temperature ac magnetic susceptibility for compounds 1 (a) (Hdc = 0, f = 500, 1500 Hz, and Hac = 3 Oe), 2 (b) (Hdc = 0, f = 10 Hz, and Hac = 3 Oe), and 3 (c) (Hdc = 0, f = 1, 10, 100, 500, 1000, 1500 Hz, and Hac = 3 Oe).
within the chains increases, and the onset of ordering of the uncompensated spins further leads to the abrupt increase of the $\chi'_M T$ values. For compound 3, the 1D ribbon structures are actually composed of 1D weakly connected pentanuclear repeating units of Mn$_2$W$_2$. From this point of view, the lack of an abrupt increase of $\chi'_M T$ values for compound 3 is logical and could be further confirmed by the rough simulation of the susceptibility data by simplifying compound 3 as a linear pentanuclear Mn$_2$W$_2$ unit. On the basis of the Hamiltonian $\hat{H} = -2J\hat{S}_{\text{Mn}_1}\hat{S}_{\text{W}_1} - 2\hat{J}_{\text{Mn}_2}\hat{S}_{\text{W}_2} - 2\hat{J}_{\text{Mn}_3}\hat{S}_{\text{W}_2}$ ($J$ represents the intramolecular coupling constant of Mn–W interactions), the $\chi'_M T$ vs $T$ plot of compound 3 could be well reproduced down to 1.8 K by running the Magpack program, affording the best match of parameters: $J = -15$ cm$^{-1}$, $g = 2.0$. The simulation result further indicates that the magnetic behavior of compound 3 is actually determined by the antiferromagnetic coupled pentanuclear Mn$_2$W$_2$ unit.

Variable-field magnetization ($-70$ to $70$ kOe) was then measured for compounds 1–3 to verify their behaviors. As shown in Figure 10b,df, compounds 1 and 2 are very easily magnetized, and the magnetizations rapidly increase and reach the saturation value of 12.88 and 11.40 kOe, respectively, and the magnetizations rapidly increase and reach the saturation value of 12.95 kOe, respectively. Interestingly, the magnetization curve of compound 3 shows a 3D network with dominant antiferromagnetic couplings between Mn(II) and W(V), which promote the formation of novel peculiar ferrimagnetic (Mn$_2$W$_2$)$_n$ chains. Interestingly, the field induced metamagnetic property was observed for compound 2, and compound 3 shows an interesting 1D ribbon structure which could be considered as the 1D arrangement of Mn$_2$W$_2$ spin clusters. Although Mn$_2$W$_2$ cluster-based compounds were not isolated in the present work, the research along this line is underway, and more useful synthetic strategies will be carried out soon in our lab.

### CONCLUSIONS

In summary, three manganese(II)-octacyanotungstate(V) bimetallic compounds 1–3 were isolated by in situ or secondary assembly methods. Structural and magnetic analyses reveal that compounds 1 and 2 show a 3D network with dominant antiferromagnetic couplings between Mn(II) and W(V), which promote the formation of novel peculiar ferrimagnetic (Mn$_2$W$_2$)$_n$ chains. Interestingly, the field induced metamagnetic property was observed for compound 2, and compound 3 shows an interesting 1D ribbon structure which could be considered as the 1D arrangement of Mn$_2$W$_2$ spin clusters. Although Mn$_2$W$_2$ cluster-based compounds were not isolated in the present work, the research along this line is underway, and more useful synthetic strategies will be carried out soon in our lab.

### ASSOCIATED CONTENT

#### Supporting Information

IR spectra and X-ray crystallographic data in CIF format of compounds 1–3. CCDC reference numbers: 991486 (1), 991487 (2) and 991488 (3). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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