

Cyanide-Bridged Single-Molecule Magnet Constructed by an Octacoordinated $[W(CN)_6(bpy)]^-$ AnionJung Hee Yoon,[†] Jeong Hak Lim,[†] Hyoung Chan Kim,[‡] and Chang Seop Hong^{*†}

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Two cyanide-bridged W^V -M [M = Mn^{III} (**1**), Co^{II} (**2**)] bimetallic clusters were prepared by self-assembling a new molecular precursor $[W(CN)_6(bpy)]^-$ and the corresponding metal complexes. Compound **1** shows a tetranuclear W_2Mn_2 entity, consisting of a Jahn–Teller ion, Mn^{III} , which serves as an anisotropic source, while compound **2** exhibits a trimeric W_2Co structure. Among them, compound **1** displays slow relaxation of the magnetization, which is typical of a single-molecule magnet behavior.

The quest for new single-molecule magnets (SMMs), which show slow magnetic relaxation originating from the large total ground-state spin and uniaxial magnetic anisotropy of molecular clusters, concerns potential applications to high-density information storage materials. A reasonable synthetic approach to creating discrete molecules instead of extended networks in the search for SMMs is to choose capped cyanide (CN)-based building units $[M(CN)_pL]^{n-}$ (M = 3d metal ion; L = polydentate ligand; $p = 2-4$) as synthons. These building blocks have been extensively studied in the construction of clusters and 1D and 2D frameworks,¹ and some of them exhibited superparamagnetic behaviors.² In contrast, despite expected strong exchange coupling of 4d or 5d magnetic ions compared to 3d metal ion systems, such SMM analogues of 4d or 5d ions are still so limited; they are Mo^{III} –

Mn^{II} and Re^{II} – Mn^{II} clusters formed by $[M(CN)_pL]^{n-}$ (M = Mo^{III} or Re^{II} ; L = tridentate ligand; $p = 3$) in which an octahedral coordination sphere around the M atom is preoccupied by a tridentate ligand as a capping group.³ In this context, for the first time, we have utilized octacoordinated $[W(CN)_p(bpy)]^-$ ($bpy = 2,2'$ -bipyridine), notably including a 5d metal ion and $p = 6$,⁴ as a new useful magnetic building brick by incorporating the precursor into magnetic anisotropic metal ions. In this Communication, we present the synthesis, structures, and magnetic properties of a tetranuclear $[W(bpy)(CN)_6]_2[Mn(L)]_2 \cdot 3H_2O$ [**1**; L = N,N' -bis(2-hydroxyacetophenylidene)-1,2-diaminopropane] and a trinuclear $[W(bpy)(CN)_6]_2[Co(DMSO)_4]$ (**2**; DMSO = dimethyl sulfoxide). Among them, compound **1** exhibits a SMM behavior, which is a rare example of SMMs containing 5d metal ions.³

A stoichiometric reaction of $(AsPh_4)[W(CN)_6(bpy)]^5$ in MeCN with $[Mn(L)(H_2O)]_2(ClO_4)_2 \cdot H_2O$ ⁶ in water leads to the formation of red crystals of **1** in a yield of 79%.⁷ The IR data for **1** show characteristic CN peaks centered at 2172w, 2152vw, 2147vw, 2133vw, and 2116vw cm^{-1} . Among them, the band observed at 2172 cm^{-1} can be assigned to bridging CN groups, and the remaining bands are responsible for terminal CN groups in comparison with the IR peaks of the precursor evident at 2160w, 2151vw, 2144vw, 2134vw, and 2124vw cm^{-1} . Treatment of $(AsPh_4)[W(CN)_6(bpy)]$ with a Co^{2+} ion in MeCN in the presence of a trace of DMSO produces **2** in a yield of 40%.⁷ The distinct CN peaks occur at 2173w and 2143w cm^{-1} , suggesting the existence of a bridging mode of CN ligands.

X-ray analysis⁷ reveals that compound **1** can be viewed as a tetranuclear entity containing two W^V and two Mn^{III} centers bridged by CN and phenoxide linkages (Figure 1a).

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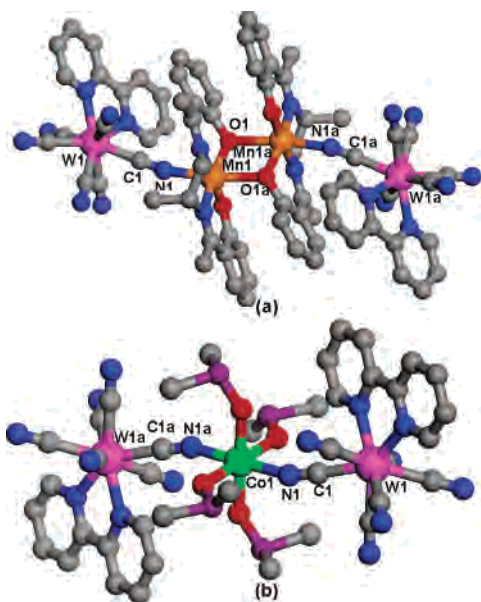


Figure 1. Molecular views of (a) **1** and (b) **2** with a selected atom-labeling scheme. Color code: W, pink; Mn, orange; Co, green; S, violet; O, red; N, blue; C, gray. Symmetry codes: $a = 2 - x, -y, 1 - z$ for **1**; $a = 1 - x, 1 - y, 1 - z$ for **2**.

The W center contains one bpy ligand and six CN groups. One among all of the CN ligands acts as a linker between W and Mn ions with a distance of 5.546(1) Å. The apical sites of a tetragonally elongated octahedral environment of the trivalent Mn ion owing to the Jahn–Teller effect are occupied by the bridging CN group [Mn1–N1 = 2.291(3) Å] and O atom from phenoxide [Mn1–O1a = 2.408(3) Å], while the equatorial positions are filled by two N and two O atoms from the Schiff base ligand with an average Mn–N(O) length of 1.93(7) Å. The intramolecular Mn–Mn separation is equal to 3.333(1) Å, and the angle of Mn–O1–Mn1a is 100.7(1)°. No π – π interactions are observed, but H bonds between lattice water O3 and free N atoms of CN ligands [O3b–N2 = 2.911(6) Å and O3b–N3c = 2.940(6) Å; $b = x, 1 + y, z$; $c = -x, 0.5 + y, 0.5 - z$] are present. The shortest intermolecular distance is 7.5280(7) Å for Mn–W. For **2**, as displayed in Figure 1b, the Co atom in an inversion center adopts a distorted octahedral geometry consisting of two N atoms from bridging CN groups [Co1–N1 = 2.138(6) Å] and four O atoms from DMSO molecules [mean Co1–O length = 2.086(1) Å]. The intramolecular Co–W distance is 5.3236(4) Å. The pyridyl rings of bpy ligands undergo intermolecular π – π contacts ranging from 3.720 to 3.965 Å (Figure S1 in the Supporting Information). The shortest intermolecular distance is 7.7282(5) Å for W–W.

For **1**, the $\chi_m T$ value of 6.78 cm³ K mol^{−1} at 300 K, as shown in Figure 2, increases smoothly and reaches to a maximum value of 14.5 cm³ K mol^{−1} at 4 K, suggesting the existence of overall ferromagnetic interactions between magnetic centers. Below 4 K, a drop in $\chi_m T$ may be relevant with zero-field splitting of a ground state and/or intermolecular interactions through the H bonds. The magnetic data

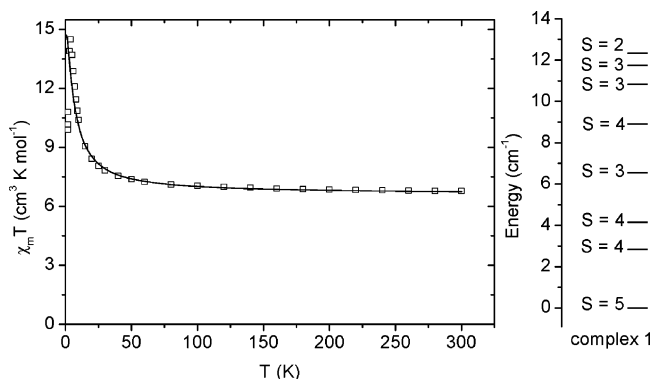


Figure 2. Plot of $\chi_m T$ vs T (left) at a field of 0.5 T and energy diagram (right) for **1**. The solid line represents the theoretical fit.

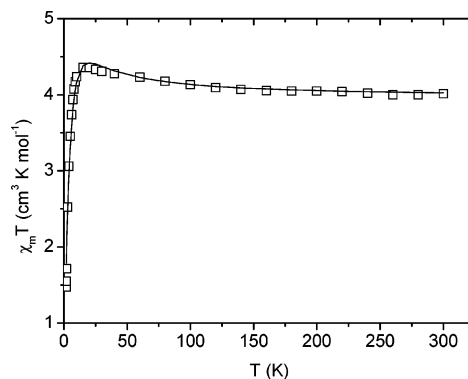


Figure 3. Plot of $\chi_m T$ vs T at 0.1 T for **2**. The solid line denotes the theoretical fit.

were simulated using *MAGPACK*⁸ on the basis of the isotropic spin Hamiltonian $H = -2J_1(S_{W1} \cdot S_{Mn1} + S_{Mn1a} \cdot S_{W1a}) - 2J_2(S_{Mn1} \cdot S_{Mn1a})$, where J_1 stands for the exchange coupling constant between W^V ($S_W = 1/2$) and Mn^{III} ($S_{Mn} = 2$) through CN and J_2 represents that between Mn^{III} ions via phenoxides. A calculated result gives $g = 1.98$, $J_1 = 0.83$ cm^{−1}, and $J_2 = 0.95$ cm^{−1}, implying that all spins in the cluster are ferromagnetically coupled. The ferromagnetic nature between CN-linked W^V–Mn^{III} and phenoxide-bridged Mn^{III} pairs in **1** is consistent with octacyanometalate-based W^V–Mn^{III} compound⁹ and Mn^{III} dimers,^{6,10} respectively. The trinuclear unit of **2** exhibits ferromagnetic interactions between W^V ($S_W = 1/2$) and Co^{II} ($S_{Co} = 3/2$) mediated by CN bridges because the gradual rise in $\chi_m T$ down to 15 K is observed (Figure 3). The exact expression of the trimeric unit (χ_m) based on an isotropic magnetic model $H = -2J(S_{W1} \cdot S_{Co1} + S_{Co1} \cdot S_{W1a})$ is indicated as

$$\chi_m = (N\beta^2 g^2 / 4kT)[A/B]$$

where $A = 1 + 10 \exp(3x) + 10 \exp(5x) + 35 \exp(8x)$, $B = 1 + 2 \exp(3x) + 2 \exp(5x) + 3 \exp(8x)$, and $x = J/kT$. A best fit with the equation under consideration of the molecular field approximation (zJ') affords parameters of $g = 2.45$ –

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(1), $J = 7.6(8) \text{ cm}^{-1}$, and $zJ' = -1.16(3) \text{ cm}^{-1}$. The exchange parameters are overestimated because of the presence of spin-orbit-coupling effects. The weak antiferromagnetic coupling between molecules can be mediated via the π - π interactions.

The $M(H)$ data for **1** increase sharply at low fields and then monotonically to a value of $7.65 \mu_B$ at 7 T, which is not saturated to the expected one ($10 \mu_B$ when $g = 2$) possibly because of an incomplete population on the ground state (Figure S2 in the Supporting Information). For **2**, the saturation value at 7 T corresponds to $4.91 \mu_B$, comparable to the ferromagnetic ground state among two W ($S_W = 1/2$) and one Co^{II} ($2-3 \mu_B$) spins (Figure S3 in the Supporting Information).¹¹

The abrupt decrease in $\chi_m T$ for **1** is associated with zero-field splitting, which is ascertained by the non-superimposed magnetization data (Figure S4 in the Supporting Information). Attempts to extract reasonable zero-field-splitting parameters from the data proved unsuccessful because of the low-lying first excited state that lies 2.83 cm^{-1} above an $S = 5$ ground state, as illustrated in Figure 2.¹² To probe the slow relaxation of the magnetization, ac magnetic susceptibilities are measured at zero dc field and an ac field of 5 G. For **1**, increasing the oscillating frequency (f) makes maxima at T_p in the in-phase component (χ_m') shift toward higher temperatures (Figure S5 in the Supporting Information), where T_p can be obtained by Lorentzian fitting. A quantity, defined as $\Delta T_p / [T_p \Delta(\log f)]$, is calculated to be 0.14, revealing that **1** behaves as a superparamagnet.¹³ The cusp temperature of the out-of-phase term (χ_m'') in the ac magnetic data is also varied against the frequencies (Figure 4). The relaxation behavior can be assessed by employing the Arrhenius law of $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$ where $\tau = 1/2\pi\nu$. A linear fit of maxima in χ_m'' leads to $\tau_0 = 5.1 \times 10^{-12} \text{ s}$ and $U_{\text{eff}} = 32 \text{ K}$, in good agreement with typical SMM behaviors.^{7,12,14} Provided that the slow relaxation emanates from the $S = 5$ ground state, the zero-field-splitting parameter (D) is estimated to be about -1.3 K , which is well compatible with the reported value for a Mn^{III} dimer.¹⁵ The Cole-Cole plot at 2.0 K gives a

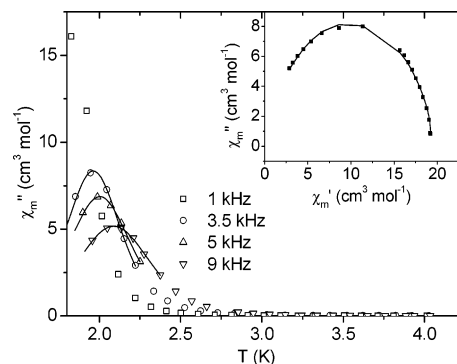


Figure 4. Plot of χ_m'' vs T at various frequencies of **1**. The solid lines are drawn by the Lorentzian peak function fitting. The inset shows the Cole-Cole diagram, where the solid line is a best fit of the data to a generalized Debye model.

semicircle, and a best fit with a generalized Debye model affords $\chi_S = 0.63 \text{ cm}^3 \text{ mol}^{-1}$, $\chi_T = 20.1 \text{ cm}^3 \text{ mol}^{-1}$, $\tau = 6.0 \times 10^{-5} \text{ s}$, and $\alpha = 0.11$ (inset of Figure 4), supporting a distribution of single relaxation processes.¹⁶ In the case of **2**, there is no frequency dependence in χ_m'' (Figure S6 in the Supporting Information).

In summary, we have prepared and characterized two bimetallic clusters constructed by $[\text{W}(\text{CN})_6(\text{bpy})]^-$ and magnetic anisotropic metal ions, and **1** exhibits slow relaxation of the magnetization. The successful application of the new capped precursor involving a 5d metal ion would open an opportunity to build up designed SMMs with improved properties.

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Supporting Information Available: X-ray crystallographic files in CIF format and additional synthetic, structural, and magnetic data for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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