A Cyanide-Bridged Single Molecule Magnet Constructed by Octacoordinated $[W(CN)_6(bpy)]^-$ Anion

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Preparations

$[W(bpy)(CN)_6]_2[Mn(L)]_2{\bullet}3H_2O$ (**1**): $(AsPh_4)[W(CN)_6(bpy)]$ (0.091 mmol) dissolved in MeCN (15 mL) was added to a suspension of $[MnL(H_2O)]_2(ClO_4)_2{\bullet}H_2O$ [L = N,N'-bis(2-hydroxyacetophenylidene)-1,2-diaminopropane] (0.046 mmol) in water (15 mL) with stirring for 20 min. The resultant clear violet solution was allowed to stand without perturbation in the dark, giving white and red crystals at the same time. The red crystals are collected by washing with MeCN and dried in air. Yield: 79%. Anal. Calcd for $C_{35}H_{31}MnN_{10}O_3W$: C, 47.85; H, 3.56; N, 15.94. Found: C, 47.49; H, 3.31; N, 16.18.

$[W(bpy)(CN)_6]_2[Co(DMSO)_4]$ (**2**): Addition of $(AsPh_4)[W(bpy)(CN)_6]$ (0.16 mmol) in MeCN (15 mL) to $Co(NO_3)_2{\bullet}6H_2O$ (0.080 mmol) in MeCN (15 mL), followed by DMSO (1 mL), afforded a red solution that was stirred for 1h. The filtered solution was left undisturbed in the dark, providing red crystals after 2 days. The crystals was washed with MeCN and dried in air. Yield: 40%. Anal. Calcd for $C_{40}H_{40}CoN_{16}O_4W_2$; C, 35.23; H, 2.96; N, 16.43. Found: C, 35.14; H, 2.85; N, 16.39.

Table S1. Crystallographic Data for **1** and **2**

	1	**2**
chem formula	$C_{35}H_{31}MnN_{10}O_3W$	$C_{20}H_{20}Co_{0.5}N_8O_2S_2W$
formula weight	878.49	681.88
crystal system	monoclinic	triclinic
space group	$P2_1/c$	P-1
a (Å)	13.0326(4)	8.8017(3)
b (Å)	13.2676(4)	10.7152(4)
c (Å)	20.8505(7)	14.1133(5)
α (°)	90	77.0020(10)
β (°)	91.7410(10)	77.5210(10)
γ (°)	90	74.4800(10)
V(Å^3)	3603.6(2)	1232.31(8)
Z	4	2
d_{calc} (g cm^{-3})	1.619	1.838
μ (mm^{-1})	3.589	5.215
F(000)	1736	663
θ range (°)	1.56 to 28.38	1.50 to 28.36
reflections collected	57261	20048
unique reflections	8869	6050
no. of parameters	458	305
R1^a [I>2σ(I)]	0.0318	0.0484
wR2^b [I>2σ(I)]	0.0722	0.1001

$^a R1=\Sigma||F_O|-|F_C||/\Sigma|F_C|$, $^b wR2 = [\Sigma w(F_O^2 - F_C^2)^2/\Sigma w(F_O^2)^2]^{1/2}$.

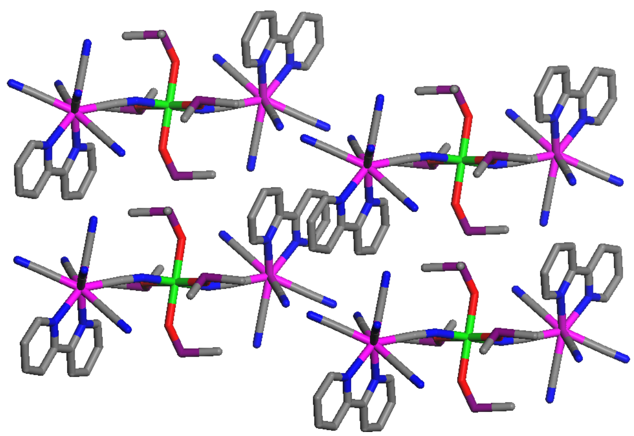


Figure S1. Extended structure of **2** showing intermolecular π-π interactions.

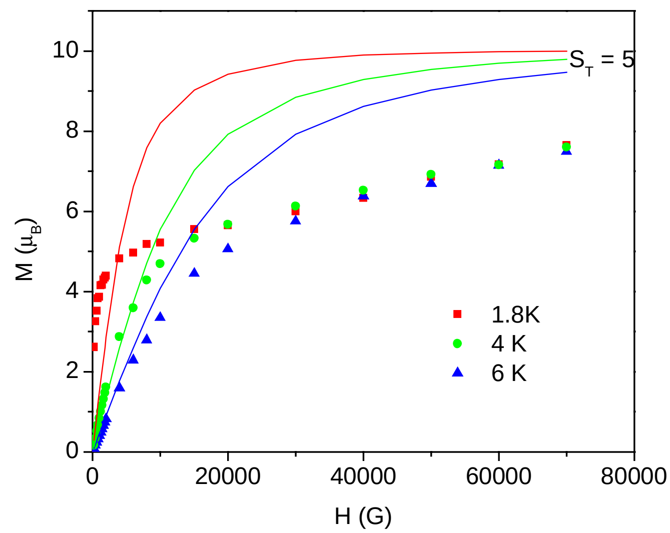


Figure S2. Plots of M versus H for **1**. The solid lines represent the Brillouin curves calculated from $S_T = 5$. The colors indicate temperatures of 1.8 K (red), 4 K (green), and 6 K (blue). At 4 K, the magnetization data at fields up to 0.8 T coincide with the Brillouin curve.

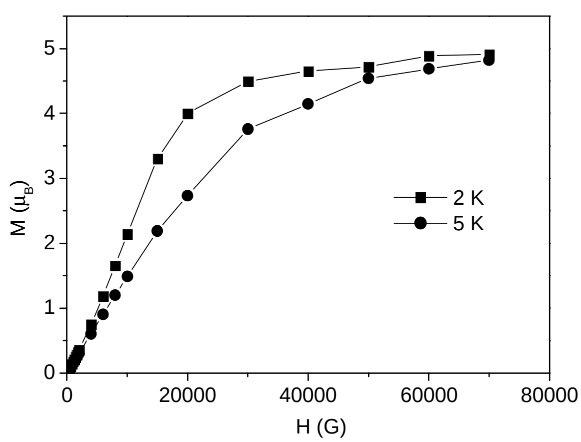


Figure S3. Plot of M versus H for **2** at 2 and 5 K.

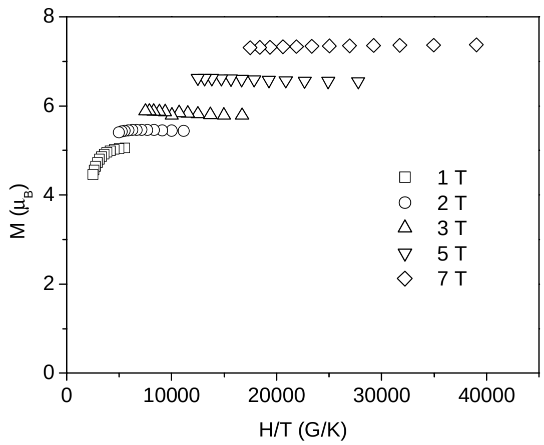
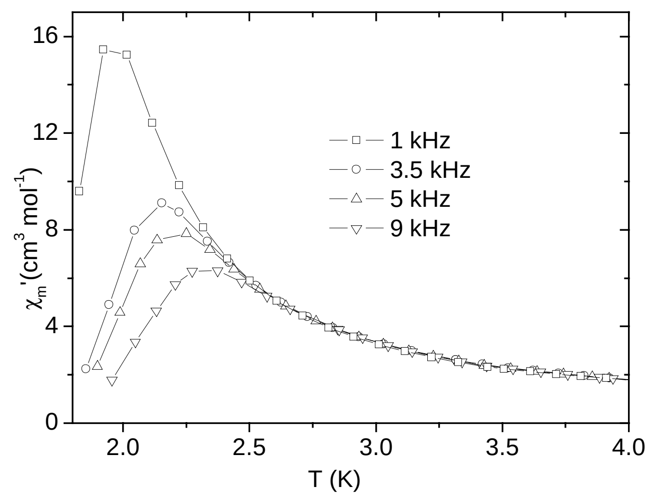
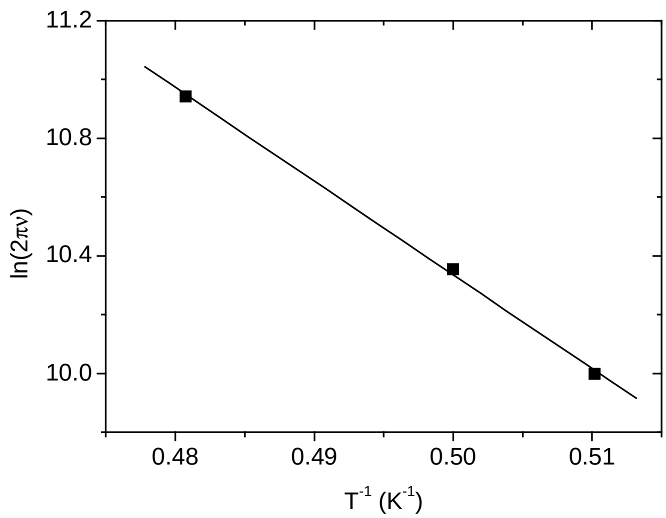


Figure S4. Plot of the magnetization M versus the ratio of the magnetic field H to temperature (T = 1.8 ~ 4.0 K) for **1**. The M is decreasing with H/T at 2 - 4 T. They are unusual and perhaps there are very weak antiferromagnetic interactions between molecules.



(a)



(b)

Figure S5. (a) In-phase ac susceptibility data (χ_m') versus temperature plot for **1** at the indicated frequencies. (b) Arrhenius plot for **1**. The solid line stands for the least-squares fit of maximums in χ_m" to the Arrhenius equation.

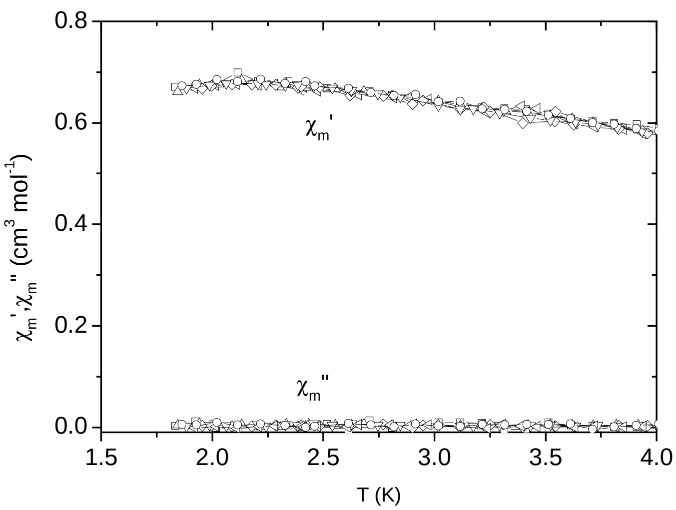


Figure S6. In-phase (χ_m') and out-of-phase (χ_m") ac susceptibility data for **2** in the frequency range of 500 – 9000 Hz in an ac field of 10 G.

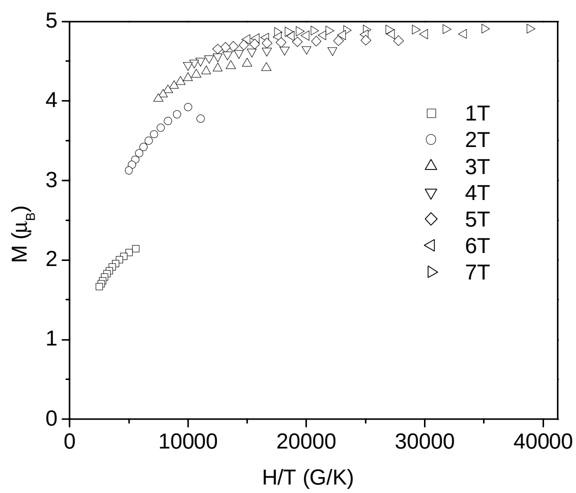


Figure S7. Plot of the magnetization M versus the ratio of the magnetic field H to temperature (T = 1.8 ~ 4.0 K) for **2**. The non-superimposed magnetization data reveal the existence of zero-field splitting arising from the octahedral Co(II) ion. The M is decreasing with H/T at 2 T. They are unusual and there are very weak antiferromagnetic interactions between molecules.