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Note

Pentanuclear Octacyanotungstate(V)-Based Molecule with a High Spin Ground State $S = {}^{13}/_2$

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Introduction

The design and synthesis of new molecule-based magnets is a very active area in chemistry because of their polyfunctional solid-state properties including light- and pressure-tuning of magnetization.[1] Among these, the design of single molecule magnets (SMMs) composed of large metal clusters is receiving special attention. Part of this interest is directed toward potential high-density information storage. The interesting magnetic behavior of SMM is due to the combination of two factors: a large spin ground-state S and a large and negative (axial) anisotropy of the ground state. The most famous examples of such discrete molecular clusters are Mn_{12} and Fe_8, which exhibit hysteresis loops with quantum steps at very low temperatures.[2] Cyanometalate complexes attract considerable interest in view of their potential in the design of SMM. A high spin ground state $S = {}^{27}/_2$ has been reported for the hexacyanometalate-based compound $[Cr^{III}(CNMn^{II}L_5)_6]^{9+}$, L_5 = trispicmeen (trispicmeen = *N*,*N*,*N*′-tris(2-pyriolylmethyl)-*N*′-methylethane-1,2-diamine),[3a] dmptacn (dmptacn = 1,4-bis(2-methylpyriolyl)-1,4,7-triazacyclononane),[3b] or tetren (tetren = tetraethylenepentaamine).[4] Very recently, two clusters based on octacyanometalate precursors $[M(CN)_8]^{3-}$ with a high spin ground state have been both structurally and magnetically characterized: $Mn^{II}_9[W^V(CN)_8]_6{\cdot}24C_2H_5OH$ with $S = {}^{39}/_2$[5] and $Mn^{II}_9[Mo^V(CN)_8]_6{\cdot}24CH_3OH$ with $S = {}^{51}/_2$.[6] These are the two highest ground state spin molecules reported to date. However, neither of these two clusters exhibit properties of SMM, because of their high, roughly octahedral symmetry. These observations prompted us to explore the possibility of lowering the symmetry of the octacyanotungstate(V)-based cluster by using the *cis*-$[Mn^{II}(bpy)_2(H_2O)_2]^{2+}$ precursor inspired from the results obtained in construction of hexanuclear clusters $[Mn(bpy)_2]_4[M(CN)_8]_2{\cdot}8H_2O$ [M = Mo(IV) or W(IV)].[7]

In this contribution, we report on the structure and magnetic properties of a new pentanuclear $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^V(CN)_8]_2{\cdot}7H_2O$ complex.

Experimental Section

Preparations. The molecular precursors $K_3[W^V(CN)_8]{\cdot}1.5H_2O$[8] and *cis*-$[Mn^{II}(bpy)_2Cl_2]{\cdot}2H_2O{\cdot}EtOH$[9] were synthesized according to the published procedures. Brown crystals of $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^V(CN)_8]_2{\cdot}7H_2O$, **1**, were grown reproducibly by slow diffusion of the aqueous solutions of *cis*-$[Mn^{II}(bpy)_2Cl_2]{\cdot}2H_2O{\cdot}EtOH$ (0.075 mmol, 39 mg, 0.3 mL) and $K_3[W^V(CN)_8]{\cdot}1.5H_2O$ (0.05 mmol, 26.8 mg, 0.3 mL) in an H-tube at room

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temperature. After one month, the crystals were filtered off, washed with water and ethanol, and air-dried. Yield: 17 mg, 30%. The molecular formula was determined by means of X-ray diffraction and elemental analysis (Found for $C_{76}H_{66}Mn_3N_{28}O_9W_2$: C, 44.6; N, 18.8; H, 3.0. Calcd: C, 44.6; N, 19.1; H, 3.2). IR: 3437s(br), 3230s, 3111m, 3088m, 2169m, 2143w, 2121w, 1632m(br), 1603s, 1595s, 1576m, 1563m, 1491m, 1474s, 1442vs, 1318m, 1244m, 1218w, 1176w, 1159m, 1118w, 1103w, 1064w, 1044w, 1017s, 975w, 900w, 815w, 766s, 737s, 651m, 627m, 463w cm^{-1}. Because of the photosensitivity of the octacyanotungstate(V) ion,[10] the reaction and the final product should be protected from light. All manipulations and measurements were carried out in red light.

Physical Measurements. IR spectra were recorded between 4000 and 250 cm^{-1} on a Bio-Rad FTS 165 FT-IR spectrometer using KBr pellets. Direct current magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID susceptometer equipped with a 5 T magnet and operating in the temperature range from 1.8 to 300 K on a collection of small crystals. The low-temperature measurements were made using magnetometers developed at the CRTBT and L. Néel laboratories in Grenoble. The high-field low-temperature SQUID magnetometer can measure absolute values of magnetization and susceptibility in fields up to 8 T and at temperatures down to 70 mK. The very sensitive micro-SQUID array magnetometer operates in fields up to 1.4 T and at temperatures as low as 40 mK. The calculations of the energy levels were made using the computer program CLUMAG.[11]

Crystallographic Data Collection and Structure Determination. Crystal data were collected at room temperature on a Nonius CAD4 diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). No significant variations were observed in the intensities of two checked reflections during data collections. Absorption corrections were applied using the Ψ-scan method. The structure was solved by direct methods using SHELXS-86.[12] All remaining non-hydrogen atoms were found by electron density map calculations. Their atomic coordinates were refined by full matrix least squares on *F*. Computation was performed by the PC version of Crystals.[13] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed at calculated positions and given a common isotropic temperature factor. Crystallographic data and details of refinement are reported in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and Discussion

The crystal structure of $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\cdot 7H_2O$, **1**, consists of pentameric molecules of slightly distorted V-shape with an alternating sequence of $Mn^{II}-W^{V}-Mn^{II}-W^{V}-Mn^{II}$ atoms and H_2O molecules (Figure 1). In the molecule, the central $[Mn(bpy)_2]^{2+}$ moiety (located on the C_2 axis) is bound to two octacyanotungstate(V) ions through a single cyano bridge. Each of the $[W(CN)_8]^{3-}$ groups is coordinated also to a terminal $[Mn(bpy)_2(H_2O)]$ moiety through a single cyano bridge. The Mn atoms are hexacoordinate and present a distorted octahedral geometry. The $[Mn(bpy)_2]^{2+}$ moiety contains either two cis cyano bridges in the central Mn unit or a single cyano bridge and an aqua ligand in a cis arrangement in the terminal one. The bond lengths and angles in the $[Mn(bpy)_2]^{2+}$ are practically identical to those found in $[Mn(bpy)_2Cl_2]\cdot 2H_2O\cdot EtOH$.[9] Each W atom has two bridging and six terminal cyano ligands arranged in a square antiprismatic geometry (D_{4d}) slightly distorted toward a bicapped trigonal prism geometry (C_{2v}). The mean W−C and C−N distances are 2.158 and 1.15 Å, respectively. Within experimental error, there are no dimensional differences between the mean values for the bridging and terminal cyano ligands. The W−C and W−N distances are in the range typical for other, isolated and bridging, octacyanotungstates(V).[5,6,14−16] The bridging CN ligands exhibit almost linear W−C−N units (maximum deviation from linearity of 5.4°) and significantly bent Mn−N−C sequences [163.7 and 162.7° for Mn(2)−N(7)−C(7) and Mn(1)−N(4)−C(4), respectively], typical for cyano-bridged octacyanides.[5,6,15,16]

Table 1. Crystal Data for $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\cdot 7H_2O$

empirical formula	$C_{76}H_{66}Mn_3N_{28}O_9W_2$
fw	2044
space group	$C2/c$
a	31.161(4) Å
b	11.247(4) Å
c	24.507(4) Å
β	95.21(1) °
V	8533(3) Å^3
Z	4
d(calcd), g cm^{-3}	1.59 g cm^{-3}
μ(Mo Kα), cm^{-1}	32.2
T, K	295
R1, wR2[a] [$I > 3\sigma(I)$]	0.051, 0.063

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = w'[1-((|F_o| - |F_c|/6\sigma(F_o))^2]^2$ where $w' = 1/\Sigma r A_r T_r(X)$ with 3 coefficients 7.25, 0.21, 5.00 for a Chebyshev polynome in which *X* represents the ratio F_o/F_c(max).

In the crystal, the V-shaped molecules are packed into infinite columns along the z direction, because of head-to-head and arm-to-arm $\pi-\pi$ stacking of the bpy rings of the terminal (“arms” of the pentamer) and central (“head” of the pentamer) Mn atoms of neighboring molecules with a distance of about 4 Å from each other. Such an arrangement leads to a chainlike structure along the y direction consisting of columns of pentamers clutched alternately with their “heads” and “arms” (Figure 2a) forming linear tubes, where H_2O molecules are located (Figure 2b). The intermetallic intermolecular distances are relatively small, being 7.4 Å between one tungsten atom and the terminal manganese atom of the neighboring molecule. The parallel-clinging orientation of pentanuclear molecules in the network gives rise to the anisotropy of the crystal.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2 \cdot 7H_2O$

Mn(1)−N(11)	2.249(7)	N(4)−Mn(1)−N(11)	86.8(3)	N(4)−Mn(1)−N(12)	91.0(2)
Mn(1)−N(12)	2.251(6)	N(4)−Mn(1)−N(21)	164.2(3)	N(4)−Mn(1)−N(22)	91.5(2)
Mn(1)−N(21)	2.253(7)	N(4)−Mn(1)−O(1)	93.1(2)		
Mn(1)−N(22)	2.225(6)	N(11)−Mn(1)−N(12)	73.1(3)	N(11)−Mn(1)−N(21)	91.4(3)
Mn(1)−O(1)	2.194(5)	N(11)−Mn(1)−N(22)	96.8(3)	N(11)−Mn(1)−O(1)	173.2(2)
Mn(1)−N(4)	2.222(6)	N(12)−Mn(1)−N(21)	103.4(3)	N(12)−Mn(1)−N(22)	169.5(2)
		N(12)−Mn(1)−O(1)	100.1(2)	N(21)−Mn(1)−N(22)	73.1(2)
		N(21)−Mn(1)−O(1)	90.5(2)	N(22)−Mn(1)−O(1)	89.9(2)
		Mn(1)−N(4)−C(4)	162.7(6)	(bridge)	
W(1)−C(1)	2.144(7)	C(1)−N(1)	1.15(1)	W(1)−C(1)−N(1)	176.4(8)
W(1)−C(2)	2.150(7)	C(2)−N(2)	1.16(1)	W(1)−C(2)−N(2)	178.4(8)
W(1)−C(3)	2.157(9)	C(3)−N(3)	1.15(1)	W(1)−C(3)−N(3)	178.1(8)
W(1)−C(4)	2.175(7)	C(4)−N(4)	1.139(9)	W(1)−C(4)−N(4)	179.3(6)
W(1)−C(5)	2.173(7)	C(5)−N(5)	1.136(9)	W(1)−C(5)−N(5)	174.6(6)
W(1)−C(6)	2.132(9)	C(6)−N(6)	1.16(1)	W(1)−C(6)−N(6)	177.4(9)
W(1)−C(7)	2.151(7)	C(7)−N(7)	1.159(9)	W(1)−C(7)−N(7)	177.7(6)
W(1)−C(8)	2.183(7)	C(8)−N(8)	1.146(9)	W(1)−C(8)−N(8)	178.4(6)
		Mn(2)−N(7)−C(7)	163.7(6)	(bridge)	
Mn(2)−N(31)	2.284(7)	N(7)−Mn(2)−N(31)	103.5(2)	N(7)−Mn(2)−N(31′)[a]	90.1(2)
Mn(2)−N(32)	2.264(6)	N(7)−Mn(2)−N(32)	87.9(2)	N(7)−Mn(2)−N(32′)	162.2(2)
Mn(2)−N(7)	2.192(6)	N(7)−Mn(2)−N(7′)	93.7(3)	N(31)−Mn(2)−N(31′)	160.1(4)
		N(31)−Mn(2)−N(32)	72.3(2)	N(31)−Mn(2)−N(32′)	94.2(2)
		N(32)−Mn(2)−N(32′)	96.1(3)		

[a] ′ = 1 − x, $^1/_2 + y$, $^1/_2 - z$.

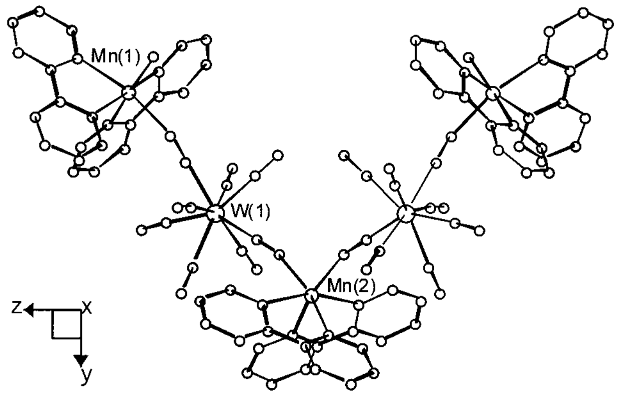

Figure 1. View of $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2 \cdot 7H_2O$, **1**, along the x-axis.

$[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2 \cdot 7H_2O$ displays three bands at 2169m, 2143w, and 2121w cm^{-1} in the IR ν(CN) stretching region. Taking into account the range 2170−2130 cm^{-1} and pattern of the ν(CN) bands of isolated octacyanotungstate(V) ion, the bands at 2169 and 2143 cm^{-1} can be attributed to the ν(CN) of terminal cyano ligands.[14b,c,17] The band at 2121 cm^{-1} can be assigned to the bridging ν-(CN) frequency. It appears that back-bonding from C-bonded W into the CN bridge increases because of enhanced removal of charge from the N end of CN to Mn, resulting possibly from electron-withdrawing [Mn(bpy)$_2$] units. These electronic effects effectively overcompensate the kinematic effect in **1** and result in slightly a lower value of bridging ν(CN) with respect to ν(CN) terminal frequencies.[13b,c,17,18]

The measured magnetization versus magnetic field of **1** measured at 2 K (squares) and the corresponding calculated Brillouin function for an $S = {}^{13}/_2$ spin system (solid line) are shown in Figure 3. The saturation magnetization is 12.7 μ_B at 2 K, close to the expected value of 13 μ_B for an antiferromagnetic coupling between three Mn^{II} ($S = {}^5/_2$) and two W^V ($S = {}^1/_2$) centers and $g_W \approx g_{Mn} \approx 2$. The magnetization curve fits well for a Brillouin function for a spin of $^{13}/_2$. The small difference between these two curves may be due to intermolecular ferromagnetic interactions and a weak anisotropy (see later). For comparison, the Brillouin function for isolated spins, three spins $^5/_2$ and two spins $^1/_2$,[19a] is shown (circles).

The temperature dependence of the product $\chi_M \cdot T$ is presented in Figure 4. At room temperature, the value of $\chi_M \cdot T$ is 12.45 cm$^3 \cdot$mol$^{-1} \cdot$K. The curve $\chi_M \cdot T = f(T)$ decreases with temperature, reaches a minimum near 60 K, and then increases rapidly to a value of 32.5 cm$^3 \cdot$mol$^{-1} \cdot$K at 2 K. The presence of a minimum in the curve confirms the antiferromagnetic interaction between the W and Mn ions. The $\chi_M \cdot T$ value at room temperature is consistent with the existence of two spins $^1/_2$ and three spins $^5/_2$ inside the molecule. The $\chi_M \cdot T$ value below 4 K is larger than that expected for isolated $S = {}^{13}/_2$ molecules (24.4 cm$^3 \cdot$mol$^{-1} \cdot$K with $g = 2$), which suggests ferromagnetic interactions between pentanuclear molecules.

To obtain an estimate of the coupling constant J between the W^V and the Mn^{II}, the isotropic Heisenberg−Dirac−Van Vleck Hamiltonian has been used:

$$\hat{H} = -J[\hat{S}_{W(1)}(\hat{S}_{Mn(1)} + \hat{S}_{Mn(2)}) + \hat{S}_{W(1)'}(\hat{S}_{Mn(1)'} + \hat{S}_{Mn(2)})]$$

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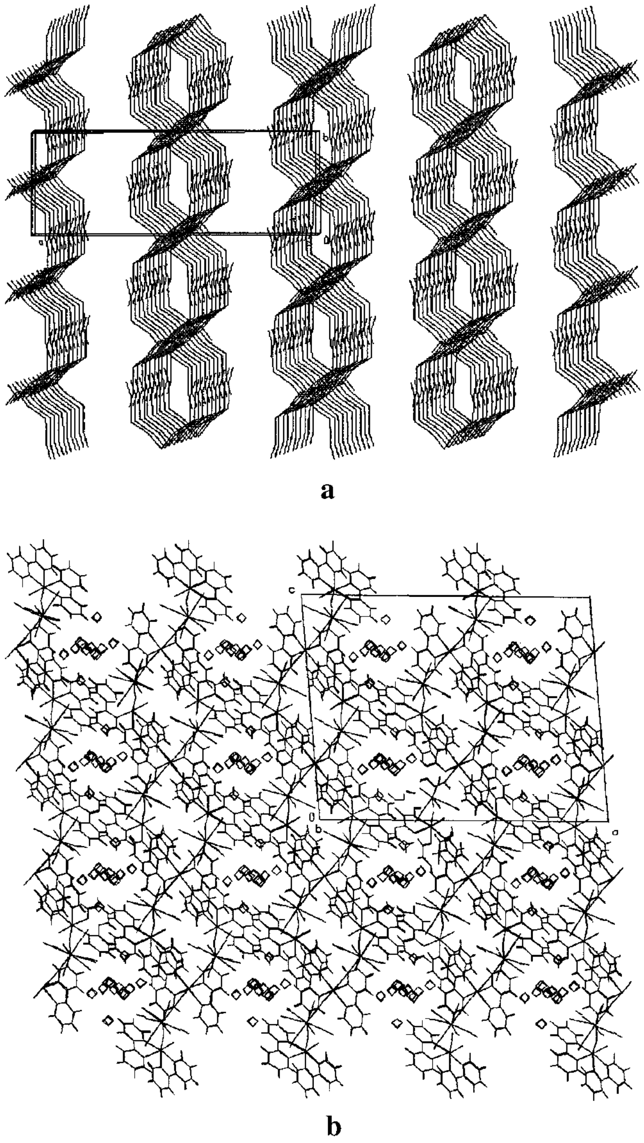

Figure 2. Part of the X-ray structure showing the packing of the molecules: (a) projection along the *z* and (b) projection along the *y* direction. The aromatic rings are omitted for clarity.

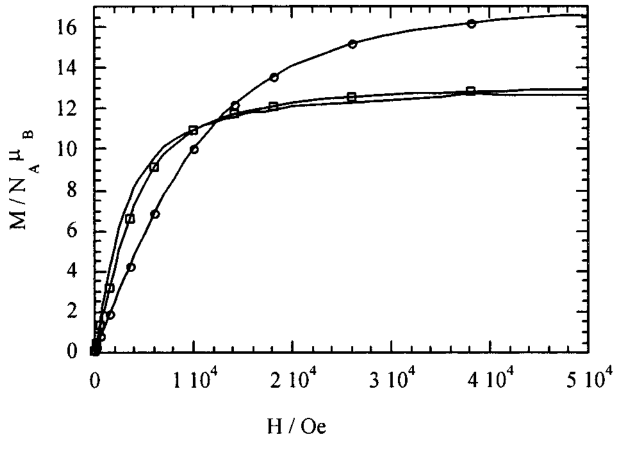

Figure 3. Magnetization of **1** vs magnetic field at 2 K: experimental, bold line; calculated Brillouin function for spin $^{13}/_2$, squares; calculated function for two independent spins $^1/_2$ and three independent spins $^5/_2$, circles.

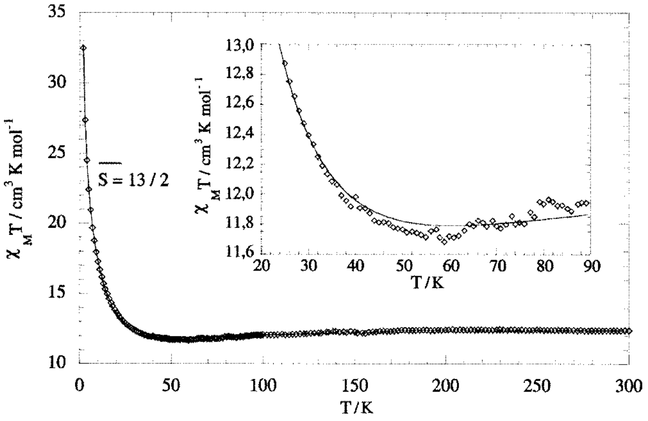

Figure 4. Thermal dependence of the product $\chi_M \cdot T$ for **1**. Insert shows an expended view of the minimum of the curve. The expected $\chi_M \cdot T$ value for an isolated spin $^{13}/_2$ is also shown.

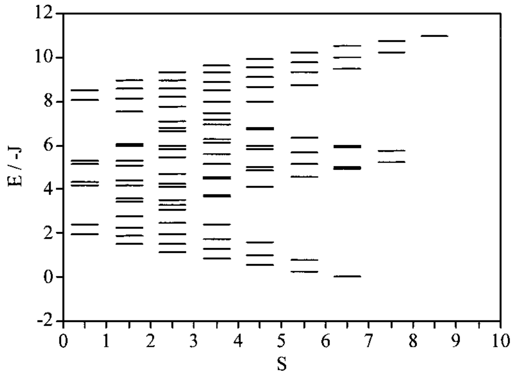

Figure 5. Energy of the different spin levels of **1** vs the spin value.

In the calculations, the following have been assumed: (i) identical antiferromagnetic interactions between W−Mn terminal and W−Mn central centers and (ii) the existence of ferromagnetic intermolecular interactions between pentameric molecules.

The energy of the different spin levels $E(S)$ as a function of J have thus been calculated. A plot of these energies as a function of J is presented in the Figure 5. The $\chi_M \cdot T$ values for one molecule have been evaluated using the Van Vleck equation:[19b]

$$\chi_{\mathrm{Mmolecule}}T = \frac{N_A g^2 \beta^2}{3k} \frac{\sum_S S(S+1)(2S+1)\exp[-E(S)/kT]}{\sum_S (2S+1)\exp[-E(S)/kT]}$$

To take into account intermolecular interactions, a mean field approximation for the susceptibility of the crystal has been used:[19c]

$$\chi_M T = \frac{\chi_{\mathrm{Mmolecule}}T}{1 - \dfrac{z\,J'\chi_{\mathrm{Mmolecule}}}{N_A g^2 \beta^2}}$$

where J' is the coupling between the neighboring molecular units, and z, the number of next neighboring molecules. The best fit has been obtained with a mean Landé factor $g = 1.95$,[20] a coupling constant $J = -12.0$ cm^{-1}, and an intermolecular coupling constant of $zJ' = +0.03$ cm^{-1}:

$$R = \sum[(\chi_M \cdot T)_{\mathrm{exp}} - (\chi_M \cdot T)_{\mathrm{calcd}}]^2 / \sum[(\chi_M \cdot T)_{\mathrm{exp}}]^2 = 0.004$$

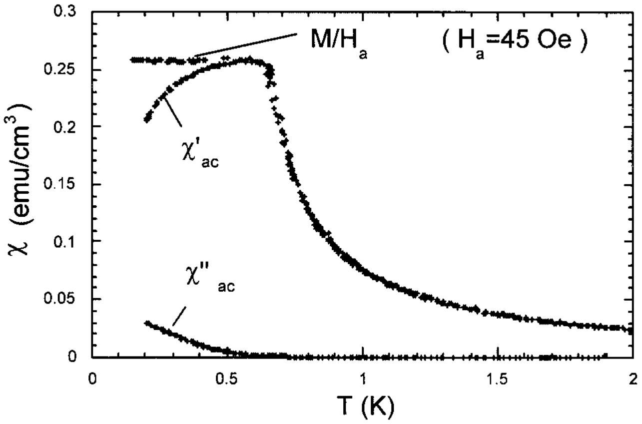

Figure 6. Direct current field cooled magnetization (normalized by the applied field $H_a = 45$ Oe) and the ac susceptibility ($f = 1.2$ Hz and $H_{ac} = 1$ Oe) at very low temperature for **1**. The sample undergoes a ferromagnetic phase transition at $T_C = 0.66$ K.

To study the magnetic properties at very low temperature, a 1 mg powder sample was prepared. To ensure good thermal contacts, small crystals were mixed with vacuum grease, and the mixture was fixed to a copper sample holder, which was attached to the bottom of the mixing chamber of a dilution refrigerator. Both ac susceptibility and dc magnetization measurements were made. Figure 6 shows the results of the field cooled magnetization normalized by the applied field (i.e., M/H_a with $H_a = 45$ Oe) and the ac susceptibility taken at a frequency of 1.2 Hz and in a field of $H_{ac} = 1$ Oe. The susceptibility increases to a value of approximately 0.25 emu/cm^3, below which a plateau appears. This very large value of the susceptibility suggests that transition to an ordered ferromagnetic phase occurs at $T_C = 0.66$ K. Indeed, the apparent susceptibility at a ferromagnetic transition should saturate to a value of $1/N$, where N is the demagnetization coefficient, and for this powder sample, N may be approximated by $N = 4\pi/3$. Measurements at different frequencies show that the transition temperature depends only weakly on frequency, and below T_C, a small imaginary part of the ac susceptibility appears.

Measurements of M versus H for various isotherms are shown in Figure 7 and were made on a single crystal weighing a few micrograms. The measurements were made by placing the small crystal directly on top of an array of micro-SQUIDs. The data were normalized by the value of the saturation magnetization measured at $T = 0.05$ K and $H = 1.4$ T. No hysteresis was seen down to the lowest temperature, 50 mK. However, a spontaneous magnetization develops below T_C, as can be seen in the figure. Here, the spontaneous magnetization may be approximated by the departure of the initial magnetization from the slope of the line $M/H = 1/N$, where again N is the demagnetization coefficient for the single crystal. These results confirm that long-range ferromagnetic order occurs below $T_C = 0.66$ K

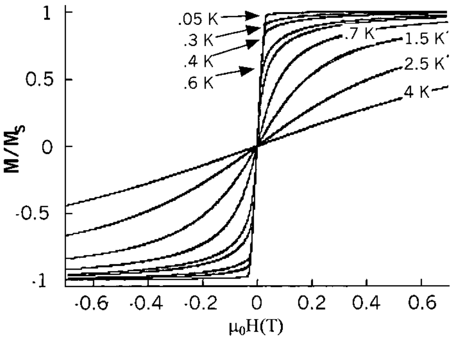

Figure 7. M vs H at various temperatures above and below T_C. The data have been normalized by the saturation magnetization measured at 1.4 T and 50 mK. For temperatures below $T_C = 0.66$ K, the appearance of a spontaneous magnetization can be seen, as defined as the departure of the magnetization from the initial slope where M/H saturates to a value of $1/N$.

Conclusions

This report expands the limited number of structurally characterized octacyanometalate(V) compounds of high spin ground state. The self-assembly process of *cis*-$[Mn^{II}(bpy)_2(H_2O)_2]^{2+}$ and $[W^V(CN)_8]^{3-}$ precursors results in formation of pentanuclear $[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^V(CN)_8]_2 \cdot 7H_2O$. The pentanuclear molecule has the slightly distorted V-shape with two tungsten(V) atoms linked by single cyano bridges to three manganese(II) centers in alternating sequence Mn−W−Mn−W−Mn. In the crystal, the parallel orientation of the molecules due to aromatic $\pi-\pi$ stacking of bpy rings results in broken chainlike structure and anisotropy of the crystal. The dc magnetic measurements between 2 and 300 K show that the complex exhibits intramolecular antiferromagnetic coupling with a coupling constant $J = -12.0$ cm^{-1} consistent with a ground spin state of $^{13}/_2$. Magnetic measurements at very low temperatures reveal that the compound exhibits long-range magnetic ordering below $T_C = 0.66$ K, thus preventing the observation of SMM behavior. Nevertheless, the results reported here suggest the possibility of designing a single molecule magnet based on octacyanometalates. Construction of clusters with reduced intermolecular interactions by the introduction of large counterions into a charged cluster-ion network may lead to a large magnetic anisotropy. Further studies are currently in progress along this line.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The g value less than 2 can be encountered in dinuclear complexes $S = {}^1/_2$ and $S = {}^5/_2$ and is related to the fact that the g tensor of the molecule is a linear combination of local tensors with a negative value of the constant of $S = {}^1/_2$ (Gateschi, D.; Bencini, A. *EPR of exchange coupled systems*; Springer: Berlin, 1990; p 53 and 55). A similar phenomenon can hold here in the pentanuclear molecule W_2Mn_3, which can explain the mean value less than 2.