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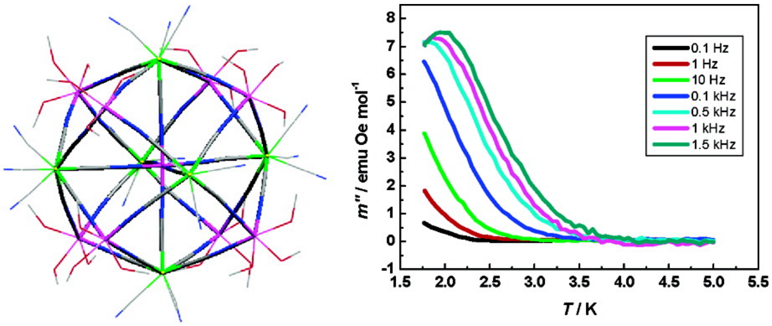

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Octacyanometallate-Based Single-Molecule Magnets: $Co^{II}_9M^V_6$ (M = W, Mo)

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Single-molecule magnets[4a] (SMMs) have been the focal point in the magnetochemistry field for intense study of quantum tunneling and slow relaxation of the magnetization in the past decade. To understand the correlation between the structure and magnetic properties, this family of SMMs is rapidly growing. Up to date, the single-molecule magnet behavior has been observed in the complexes, including Mn, Fe, V, Co, Ni[1], or rare earth.[2] In these SMM structures, most consist of a metal−oxo or carboxylate cluster core. CN group, as the very efficient bridge mediating the strong magnetic coupling interaction between metal ions, is scarcely introduced in the SMMs[3] due to the difficulty in the design and the synthesis for the superparamagnetic cluster containing the first transition metal ions. Hasimoto's and Decurtins' groups first synthesized octacyanometallate-based clusters with high spin[4] utilizing $W^V(CN)_8{}^{3-}$ and $Mo^V(CN)_8{}^{3-}$ as the building blocks, respectively, but no available evidence was obtained for their single-molecule magnetic behavior in the physical measurements. It is suggested that the Mn(II) ion is not a good candidate for SMMs. However, investigating the magnetism of octacyanometallate-based clusters is obviously significant for SMMs due to the relative high spin ground states. For observing possible single-molecule magnetic properties in this system, we tried introducing the atoms with anisotropy and spin−orbital coupling into the superparamagnetic cluster, such as substituting Co(II) ions or lanthanide for Mn(II) ions, and synthesized two novel octacyanometallate-based clusters, $\{Co^{II}_9[W^V(CN)_8]_6\cdot(CH_3OH)_{24}\}\cdot 19H_2O$ (**1**) and $\{Co^{II}_9[Mo^V(CN)_8]_6\cdot(CH_3OH)_{24}\}\cdot 4CH_3OH\cdot 16H_2O$ (**2**). Both complexes show the single-molecule magnetic properties though the structures are similar to Mn_9W_6 and Mn_9Mo_6.[4]

Both **1** and **2** were synthesized by the reaction of 2 equiv of $CoCl_2\cdot 6H_2O$ with 1 equiv of $Na_3[M^V(CN)]_8\cdot 4H_2O$ (M = W, Mo) in the methanolic solutions, below 20 °C in the dark. The dark-red well-shaped crystals for single-crystal X-ray structure analysis was obtained after several days. The crystal is highly moisture sensitive. So, all physical measurements were performed by covering liquid paraffin on the crystal.

X-ray analysis[5] reveals **1** and **2** crystallized in a lower space group than did Mn_9W_6.[4a] Both **1** and **2** are comprised of nine Co^{II} ions and six $M^V(CN)_8$ [M = W (**1**) or Mo (**2**)] ions bridged by cyanides leading to a six-capped body-centered cube (Figure 1). Two $M^V(CN)_8{}^{3-}$ ions adopt bicapped trigonal prismatic geometry, and the others favor dodecahedron. All $M^V(CN)_8{}^{3-}$ ions provide five CNs each to connect with Co^{II} ions constructing the cluster skeleton, while the remaining three CNs are terminal to face out of the cluster. Eight Co atoms are located at the corners of the cube with distorted octahedral environment, and each accepts three CN ligands for the skeleton. Other positions are occupied by methanol molecules. The ninth one is at the center of the cube, which is coordinated by six N atoms from the bridging CNs. The shortest intercluster Co···W and Co···Mo distances are 6.993 and 6.973 Å, respectively, which are comparable with that in Mn_9W_6 (7.086 Å).[4a] In fact, the spatial configurations of $M^V(CN)_8{}^{3-}$ ions and the free solvent molecules in the lattice make **1** and **2** different from Mn_9W_6[4a] in the structure and the symmetry.

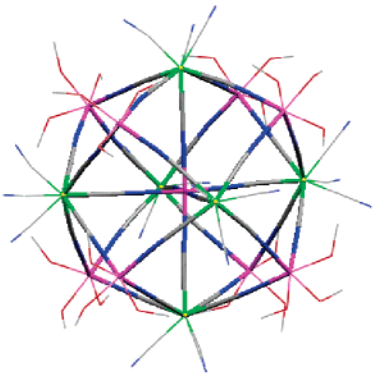

Figure 1. Structure of $\{Co^{II}_9[M^V(CN)_8]_6\cdot(CH_3OH)_{24}\}$ cluster for **1** (M = W) and **2** (M = Mo). Sphere colors: green, W or Mo; pink, Co; gray, C; blue, N; red, O.

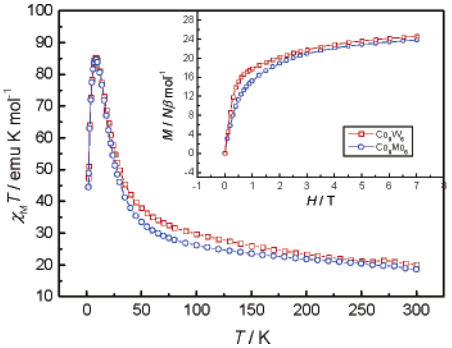

Figure 2. Plots of $\chi_M T$ versus T for **1** and **2** at a field of 0.1 kG. Insert is the field dependence of magnetization at 1.8 K. The solid line is the guide.

The magnetic susceptibilities of complexes **1** and **2** at an applied field of 0.1 kG are shown as the $\chi_M T$ versus T plots in Figure 2. For **1** at room temperature, $\chi_M T$ is 20.2 emu·K·mol^{-1}, which is slightly higher than the spin-only value of 19.13 emu·K·mol^{-1} for the $Co^{II}_9W^V_6$ unit ($S_{Co} = {}^3/_2$, $S_W = {}^1/_2$ and $g = g_{Co} = g_W = 2$). When the temperature is decreased, $\chi_M T$ gradually increases. Below 50 K, $\chi_M T$ rapidly increases and reaches a maximum of 85.2 emu·K·mol^{-1} at 8 K, and then sharply decreases below this temperature. This maximum value is higher than 60.4 emu·K·mol^{-1} based on a ground-state spin $S_T = {}^{21}/_2$ of antiferromagnetic coupling between Co^{II} and W^V ions but is much less than 144.4 emu·K·mol^{-1} on $S_T = {}^{33}/_2$ of ferromagnetic coupling. Considering the strong orbital contribution of the Co^{II} ions, which leads to an average g value that is much higher than 2, it is suggested that there is the presence of antiferromagnetic exchange between Co^{II} and W^V ions in this complex. Thus, an overall g value is estimated to be 2.37 on a basis of the maximum $\chi_M T$ and $S_T = {}^{21}/_2$. Consequentially, a

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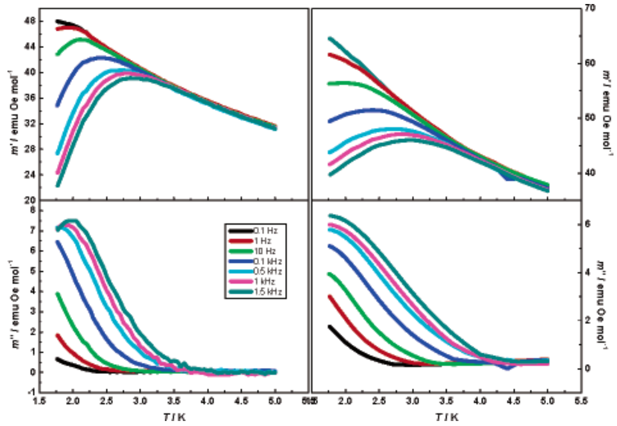

Figure 3. AC magnetic measurements for **1** (left) and **2** (right) at $H_{ac} =$ 5 G and $H_{dc} = 0$.

saturation magnetization, $M_s = gS_T = 24.9\ N\beta\ \text{mol}^{-1}$, and Curie constant, $C = 26.8$ emu·K·mol^{-1}, are obtained. The former is consistent with the observed value of 24.6 $N\beta$ mol^{-1} in the variable-field magnetic measurements at 1.8 K (insert in Figure 2). The latter is higher than the $\chi_M T$ value at room temperature because the intracluster ferromagnetic order may lead to a minimum $\chi_M T$ at a temperature higher than 300 K. Similar behavior was also observed in other octacyanometallate-based magnets.[6]

Complex **2** shows magnetic behaviors very similar to those of **1** (Figure 2), but at room temperature, $\chi_M T$ is 18.6 emu·K·mol^{-1}, which is slightly less than the theoretical value of 19.13 emu·K·mol^{-1} for $Co^{II}_9Mo^{V}_6$, and goes through the maximum of 84.6 emu·K·mol^{-1} at 9 K. At 1.8 K and 7 T, the saturation magnetization, 23.8 $N\beta$ mol^{-1}, was observed. These magnetic data all indicate the antiferromagnetic interaction between Co^{II} and Mo^{V} ions and a ground-state spin of $^{21}/_{2}$. In the variable-field magnetization measurements of **1** and **2**, there is no coercive field observed, implying a blocking temperature lower than 1.8 K.

AC magnetizations of **1** and **2** were measured and show the strong frequency dependence of both the real and imaginary part of magnetization, m' and m'', below 3 K for **1** and 4 K for **2** (Figure 3). Each m' and m'' for **1** at a selected frequency goes through a maximum, and the maxima shift to high temperature with increasing frequencies, which is a characteristic behavior of superparamagnets and slow relaxing molecular clusters. Assuming that the temperature of the maximum corresponds to the peak temperature, T_p, the frequency dependence of the peak temperature shift (ΔT_p) of m' leads to $\Delta T_p/[T_p\Delta(\log\omega)] = 0.13$,[7] further indicating complex **1** to be a superparamagnet. Equally, the T_ps in the plot of m'' versus T (T_p at a fixed frequency may be obtained by the Lorentz peak function fitting) educe a linear plot of $1/T_p$ versus $\ln(2\pi\nu)$, which is in a good agreement with the Arrhenius law, $\tau(T) = \tau_0\exp(\Delta E/k_BT)$ (Figure S1 in Supporting Information). The best fit gives the relaxation time, $\tau_0 = 7.39 \times 10^{-11}$ s, and the energy barrier, $\Delta E/k_B = 27.79$ K, which are consistent with single-molecule magnet behavior.[1a,8] Therefore, complex **1** is a new example of SMMs. To the best of our knowledge, it is the first octacyanometallate-based SMM experimentally verified. Complex **2** shows similar behavior, but the magnetic properties are not discussed in detail because observed peaks in $m''-T$ plots are not convenient for the investigation on magnetism. The additional evidence of **1** and **2** bearing the SMM behavior is the magnetization versus dc field measurements. Both plots of reduced magnetization ($M/N\beta$) versus H/T of **1** and **2** (Figures S2 and S3 in Supporting Information) show that the isofield lines do not superimpose, indicating significant magnetic anisotropy (zero-field splitting) in the ground state.

In conclusion, for the first time, we successfully introduced a Co(II) ion with anisotropy and spin−orbital coupling into an octacyanometallate system and synthesized two $Co^{II}_9M^{V}_6$ (M = W and Mo) clusters. The observed magnetic behaviors display the nature of SMMs. Comparing the magnetic properties and the structures of $Mn^{II}_9M^{V}_6$ (M = W and Mo),[4] the substitution of metal ions is obviously the main reason that **1** and **2** exhibit the SMM behaviors.

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

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(5) Crystal data for **1**: $C_{72}H_{134}N_{48}O_{43}Co_9W_6$, $M_W = 3993.74$; monoclinic; space group $C2/c$; $a = 28.764(9)$, $b = 19.258(6)$, $c = 32.519(10)$ Å; $\beta = 114.012(5)°$; $V = 16455(9)$ Å^3; $Z = 2$; $D_c = 1.612$ g/cm^3; $T = 293(2)$ K. For **2**: $C_{76}H_{144}N_{48}O_{44}Co_9Mo_6$, $M_W = 3540.40$; monoclinic; space group $C2/c$; $a = 28.72(2)$, $b = 19.276(13)$, $c = 32.49(2)$ Å; $\beta = 114.241(12)°$; $V = 16403(20)$ Å^3; $Z = 2$; $D_c = 1.434$ g/cm^3; $T = 293(2)$ K. The structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. The refinement was performed against all reflections (16 108 for **1** and 16 078 for **2**). The goodness-of-fit on F^2 is 0.970 for **1** and 1.029 for **2**. The final refinement gave R_1 (wR_2) = 0.0424 (0.0863) [for 12 261 reflections with $I > 2\sigma(I)$] for **1** and $R1$ (wR_2) = 0.0506 (0.1168) [for 12 238 reflections with $I > 2\sigma(I)$] for **2**.

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